CFTRI-MYSORE
321[illegible]
Industrial and m..

TLNS

H. VENKATARAMIAH & SONS
VIDYANIDHI BOOK DEPOT
NEW STATUE CIRCLE MYSORE

INDUSTRIAL
&
MANUFACTURING CHEMISTRY

Part II

INORGANIC

VOL. II

UNIFORM WITH THIS VOLUME

★

INDUSTRIAL
&
MANUFACTURING CHEMISTRY
PART I. ORGANIC

Seventh Edition Revised by
EDWARD I. COOKE, M.A., B.SC., A.R.I.C.

Over 800 pages and 250 illustrations

★

PUBLISHED BY
THE TECHNICAL PRESS LTD.

INDUSTRIAL
&
MANUFACTURING CHEMISTRY

Part II

INORGANIC

BY

GEOFFREY MARTIN, D.Sc., Ph.D., F.R.I.C.

Sixth Edition Revised by

WILFRID FRANCIS, M.Sc., Ph.D., F.R.I.C., F.Inst.F.
Consulting Chemist and Fuel Technologist

Assisted by

NORBERT BERKOWITZ, Ph.D.
MARCUS FRANCIS, Ph.D., F.R.I.C.
ALFRED B. SEARLE

VOLUME II

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE, * MYSORE. *
16 SEP. 1955
LIBRARY

LONDON
THE TECHNICAL PRESS LTD.
1954

First Published	1917
Second Edition	1918
Third Edition	1919
Fourth Edition (VOL. I)	1922
Fourth Edition (VOL. II)	1925
Fifth Edition	1935
Reprinted	1944
Sixth Edition	1954

3215 ✓

F8

N52.3

UNIFORM WITH THIS VOLUME

★

INDUSTRIAL
&
MANUFACTURING CHEMISTRY

PART II—INORGANIC, VOL. I

Solid Fuels: Wood and Peat—Solid Fuels: The Coal Series—Processed Solid Fuels—Liquid Fuels—Gaseous Fuels—Industrial Hydrogen—Producer-Gas and Water-Gas—The Carbon Dioxide (Carbonic Acid) Industry—Industrial Ozone—The Technology of Water—Artificial Mineral Waters—The Sulphur Industry—Sulphuric Acid—Manufacture of Sulphur Dioxide and Sulphites—Manufacture of Other Sulphur Compounds—The Salt Industry—The Manufacture of Hydrochloric Acid—The Manufacture of Sodium Sulphate (Salt Cake)—General Survey of the Sodium Carbonate Industry—The Manufacture of Sodium Carbonate and Caustic Soda by the Leblanc Process—Manufacture of Sodium Carbonate by the Ammonia Soda Process—The Stassfurt Industry—Potassium Salts—Calcium and Magnesium Salts—The Gypsum Industry—Barium Salts—Strontium Salts—Compounds of Boron—The Manufacture of Chlorine by the Weldon and Deacon Processes—Electrolytic Chlorine and Alkali—Liquid Chlorine—Manufacture of Chlorates and Perchlorates—Bleaching Powder and Hypochlorites—The Bromine Industry—The Iodine Industry—The Hydrofluoric Acid Industry—Peroxides and Peracids—The Circulation of Nitrogen in Nature—The Nitrate Industry—The Nitric Acid Industry and Nitrous Oxide—The Ammonia and Ammonium Salts Industry—Synthetic Ammonia—The Cyanamide Industry—The Cyanide and Prussiate Industry—Refrigerating and Ice-making Machinery—The Liquefaction of Gases—Industrial Oxygen—Industrial Nitrogen—Pyrometry and Pyroscopy—Principles of Combustion—Combustion Appliances.

THE TECHNICAL PRESS LTD.

Printed in Great Britain by
Neill & Co. Ltd. Edinburgh

CFTRI-MYSORE
3215
Industrial and m

PREFACE TO SIXTH EDITION

A continued demand for Martin's "Industrial Chemistry" over the past twenty years has resulted in the publication of this new edition. A new Editor has been appointed, with instructions to bring the work up to date without altering its essential character.

In order to do this in a satisfactory manner, all out-of-date matter without historical or technical significance has been replaced by new matter, but the older material relating to the classical development of processes or industries has been retained because of its great value to students, manufacturers, and commercial interests. The sections on fuel and related processes have been re-written completely, and complementary new sections added to cater for the increasing world awareness of the importance of fuel economy and to illustrate the great advances in the subject of fuel utilisation and power generation that have taken place during the past few decades.

In other major sections, sufficient new material has been included to indicate the latest developments in the various subjects and numerous references to new books and to the periodic scientific literature have been given to enable the specialised reader to obtain more details of the latest information on any subject than it has been possible to provide in the space available. This has meant, in some instances, making the larger sections a little unwieldy, though up to date. Many of the minor sections have been enlarged to include recent developments and in all cases up-to-date references are given.

In subsequent editions, also, new sections will be added from time to time, or substituted for minor sections, to keep in step with important trends in the field of chemical industry. The sections on the alkali industry have been retained in their entirety because of their great interest to students of applied chemistry, though here, also, some new information on the latest developments in this field has been included.

The publishers have been fortunate in retaining the assistance of Mr A. B. Searle, for the revision of some of his original sections, whilst the other collaborators in the new edition have specialised knowledge of the subjects in the sections that they have revised. The Editor and his collaborators invite helpful criticisms of subject matter and will be glad to have their attention called to any serious omissions or errors in any sections. As with the earlier editions, readers with difficult problems to solve relating to any of the subjects covered by the new edition are invited to communicate with the Editor for advice and help.

W. FRANCIS.

14 Albion Road,
Kingston-on-Thames.

PREFACE

A TREATISE on technical Inorganic Chemistry, which includes accounts not only of the more important industries, but also details of the minor ones, has been a long felt want amongst practical business men interested in chemical processes of manufacture.

The present work forms a continuation, or supplement, to the Editor's "Treatise on Industrial Organic Chemistry," which has evidently filled a gap in chemical literature. It embraces both British and American practice, and affords, so far as is ascertainable in view of the many secret processes employed, thoroughly up-to-date information regarding the various branches of chemical industry and of manufactures having a chemical basis.

The work, which has been carried out on the lines of the previous treatise, has been written under very formidable difficulties, for not only have several years been spent in its compilation, but before its completion the Great War broke out and dispersed many of the contributors in the fighting ranks throughout the world, one at least, the late Major L. Foucar, having been killed in action before his article could be completed. It is a great satisfaction to the Editor that he has been able to bring his task to a conclusion in spite of these obstacles.

The immensity of the subject, and the large number of industries embraced under the comprehensive title "Industrial Inorganic Chemistry," has necessitated the division of the work into two volumes.

The Editor has been fortunate in securing the co-operation of a distinguished body of contributors, all of whom are experts in their particular subjects; their names and attainments, as enumerated on the title pages of the two volumes and more specifically in the list of contents, are a guarantee that the minutest care has been exercised to ensure accurate descriptions of the industries concerned, and to these gentlemen the Editor owes a considerable debt of gratitude, and to many other professional friends who have supplied information or given help in subjects in which they have specialised.

One great difficulty in compiling such a treatise is the extraordinarily rapid advance in scientific invention in many industries. Almost overnight (so to speak) new industries arise out of improvements or inventions, the details of which it is almost impossible to procure.

In carrying out the work, however, special pains have been taken to ensure that the most recent available data, and the most modern processes, have been described. Much of the information is published in book form for the first time, and many of the descriptions of new processes and modern plant have been supplied by the courtesy of industrial chemists and leading firms of Europe and America.

Patent literature has been utilised to the fullest extent, since many patents, although impracticable, often contain the germs of valuable ideas. Indeed the Editor ventures to claim that such a copious reference given to the technical and patent literature of all countries has not appeared in any similar work published in English, and he hopes that by this means a reader who desires further details respecting any process described will be enabled, without difficulty, to refer to the original source.

The Editor's aim is to cover the whole range of subjects with which the industrial chemist and manufacturer are usually concerned, and to present a book which would serve either as a text-book or as a work of reference to meet the requirements of business men interested in chemical processes, chemists, chemical engineers, patent workers, inventors, students, and others. He trusts the work will be found to carry out this object, and that it may prove of real utility to all interested in chemical manufacture.

It should be mentioned that while the title indicates that only Inorganic Compounds are dealt with, it has been found advisable to include, in the sections on Disinfectants and Antiseptics, a number of Organic Compounds which fall naturally under these headings, since the removal of them from such sections would largely destroy their value.

Although every care has been taken in the production of the work, yet, in view of the mass of detail involved, it is impossible that all errors have been eliminated, or that in every case the best processes have been described. The Editor will, therefore, be grateful if readers will kindly inform him of any erroneous statements, or will call his attention to any serious omissions.

On the other hand, he would be pleased to help such readers who have difficulty in carrying out various processes described if they would communicate their difficulties to him.

LONDON, *December* 1916.

PREFACE TO FOURTH EDITION

THE fact that four Editions of a large work like the present have been called for after such a comparatively short interval of time indicates that the book still retains its popularity among technologists. The reason, no doubt, is due to the very great trouble which has been taken in order to keep the book thoroughly up to date. The Editor hopes that practical men will continue to favour him with suggestions for improving the work, so as to keep it as closely as possible in touch with altering practice in technology.

GRAVESEND, *July* 1922.

PREFACE TO FIFTH EDITION

THE popularity of the book continues undiminished. An attempt has been made to keep the book up to date, and the Editor hopes that practical men will continue to favour him with suggestions.

The work aims at giving a brief survey of Chemical Industry. Obviously (so extensive has technological literature become) an exhaustive account of Modern Industry would require unlimited space and defeat the object of this work.

GEOFFREY MARTIN.

LONDON, 1935.

TABLE OF CONTENTS

SECTION LII

DISINFECTANTS AND ANTISEPTICS

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

PAGE

Literature—Introduction—Distinction between Disinfectants and Antiseptics—Germicidal Power—Testing Disinfectants—The Rideal-Walker Carbolic Acid Coefficient - 1

Part I. Organic Disinfectants and Antiseptics.

Coal Tar Fluids—The Cresols—Guaiacol—Creosol—Thymol—Resorcinol—Catechol—Hydroquinone — Pyrogallol — Beta-Naphthol — Tribromnaphthol — Substituted Naphthols—Essential Oils—Eucalyptus—Pinol—Sanitas—Benzoic Acid—Salicylic Acid—Salol—Salophen—Acetic Acid—Propionic Acid—Tartaric Acid—Citric Acid—Lactic Acid—Formic Acid—Formaldehyde—Paraformaldehyde—Iodine Cyanide — Iodoform — Carbon Tetrachloride — Saccharin — Hexamethylenetetramine—Organic Dyes—Acriflavine—Dettol—T.C.P. - - - - - - - 2

Part II. Inorganic Disinfectants.

Oxidising Disinfectants—Oxygen—Ozone—Hydrogen Peroxides—**Metallic Peroxides**—Calcium Peroxide—Magnesium Peroxide—Sodium Peroxide—Zinc Peroxide—Mercury Peroxide—Persulphates —Percarbonates —Perborates —Permanganates—**Chlorine and Hypochlorites**—Break-point Chlorination of Water. **Bromine and Iodine and their Derivatives**—Bromine —Bromidine—Iodine —Iodine Trichloride. **Acids, Metallic Salts, Alkalis, and Metals** —Germicidal Power of Acids and Metallic Salts—Boric Acid —Sodium Borofluoride—Osmic Acid —Carbonic Acid—Hydrofluoric Acid and Fluorides - Hydrofluorsilicic Acid —Hydrocyanic Acid and Cyanides—Nitric Acid and Oxides of Nitrogen —Chromic Acid—Sulphuric Acid—Acid Sodium Sulphate—Sulphur Dioxide and Sulphites —Sulphur—Arsenic—Lime—Sodium and Potassium Hydroxides - Sodium and Potassium Carbonates —Soaps —Salt—Copper and Copper Salts—Mercury and Mercury Salts—Silver Salts—Zinc Salts and Zinc—Aluminium Salts and Aluminium—Iron Salts and Metallic Iron - - - - - - - - - 4

Part III. Antibacterial Drugs and Antibiotics.

Sulphonamides — Penicillin — Antimalarials — Antibiotics — Streptomycin — Other Antibiotics—References - - - - - - - - - - - - 16

SECTION LIII

FUNGICIDES, SHEEP-DIPS, AND INSECTICIDES

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

PAGE

Literature—**Copper Compounds**—Bordeaux Mixtures—Peach Bordeaux Mixture—Soda Bordeaux Mixture—Potash Bordeaux Mixture—Soap Bordeaux—Manufacture. **Sulphur Fungicides**—Sulphur—Sulphur and Resin Solution—Potassium Sulphide Fungicide—Corrosive Sublimate—Lime-Sulphur Washes—Preparation—Formaldehyde—Modern Fungicides, Insecticides, and Weed-killers. **Sheep-Dips**—Lime and Sulphur Dips—Preparation of Lime and Sulphur Dips—Use of Lime and Sulphur Dips. **Tobacco and Sulphur Dips**—Nicotine Manufacture—Preparation of Tobacco Extract for Dips. **Arsenical Dips**—Formulas—Disadvantages. **Carbolic Dips. Insecticides**—Arsenic Compounds—Derris Powder—Pyrethrum Powder—D.D.T.—Gammexane—Phosphoryl Esters—References - - - - - - - - - - - - 17

SECTION LIV

ARTIFICIAL MANURES

By A. S. Carlos, B.Sc.
Revised by Wilfrid Francis

Literature—I. **Phosphatic Manures**—Natural Phosphates—Crushing—Grinding—Ball Mills—Tube Mills—Ring Roll Mills—Roll Mills—Disintegrating Machines—Stamp Mills—Separators—Screen Separators—Air Separators—Superphosphate—Process of Manufacture—Milch Patent Superphosphate Den—Milch Chamber—Basic Superphosphate—Double Superphosphate—Dissolved or Vitriolised Raw Bones—Dissolved Bone Compounds—Basic Slag. II. **Phospho-Nitrogenous Manures**—Bones—Raw and Unsteamed Bone Manure—Crushing—Steamed or Gelatinised Bones—Flesh Meal—"Fray-Bentos" Guano—Fish Manures or Guanos—The Drier—Wet Fish Scrap—Whale Meal. III. **Nitrogenous Manures**—(a) *Inorganic*—Nitrate of Soda—Ammonium Sulphate—Calcium Nitrate. (b) *Organic*—Calcium Cyanamide—Nitrolim—Rape Cakes and Meals—Rape Seed Meal—Castor Oil Meals—Blood Meal—Horn and Hoof Meals—Wool, Shoddy, Rags, etc.—Skin and Leather Meals—Bacterial Manures—Use of Waste Products for Making Manures. IV. **Potash Manures**—Agricultural Consumption of Potash in the World—Chief Potash Manures: Kainit—Muriate of Potash—Sulphate of Potash—Nitrate of Potash. V. **Miscellaneous Manures**—Salt—Calcium or Lime Manures—Quicklime—Calcium Carbonate—Silicate Manures. VI. **Mixed Manures**—Potassic Superphosphate—Saltpetre Superphosphate—Artificial Guano. VII. **Guanos**—(a) Raw Peruvian Guano—Lobos Guano. (b) Rectified Guano—Products obtained from Sewage Sludge, Town Refuse, etc. VIII. **The Fertilisers and Feeding Stuffs Act**, 1906—Limits of Error—Analysis of Manures: 1. **Determination of Moisture**. 2. **Determination of Nitrogen**: Nitrogen in the Absence of Nitrates—Nitrogen when Nitrates are Present—Nitrogen in the Form of Ammonium Salts—Nitrogen in Nitrates in the Absence of Ammonium Salts and of Organic Nitrogen—Control Experiments in the Determination of Nitrogen. 3. **Determination of Phosphates**: Phosphates Soluble in Water—Phosphates Soluble in the Prescribed Citric Acid Solution—Total Phosphoric Acid—Molybdate Method—Preparation of Molybdic Acid Solution—Preparation of Magnesia Mixture—Preparation of Ammonia Solutions. 4. **Determination of Potash**: Muriate of Potash Free from Sulphates—Salts of Potash Containing Sulphates—Potash in Guanos and Mixed Fertilisers—Forms of Certificates. The Fertilisers and Feeding Stuffs Act, 1926. Statistics—Availability of Nitrogenous Fertilisers—World Production and Consumption of Fixed Nitrogen—References - 73

SECTION LV

THE INDUSTRY OF ALUMINIUM COMPOUNDS

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

PAGE

Literature—Manufacture of Aluminium Hydroxide and Alumina—The Dry Process—The Wet Process. **Manufacture of Alumina and Aluminium Hydroxide from Cryolite**—Cryolite—Manufacture of Alumina from Aluminium Nitride—Properties and Use of Aluminium Hydroxide and Alumina—Anhydrous Alumina—Fused Alumina as a Grinding Agent—Alumina in the Manufacture of Artificial Rubies and Sapphires—Use of Bauxite, Kaolin, and Cryolite in the Manufacture of Aluminium Sulphate—Manufacture from Bauxite. **Manufacture of Aluminium Sulphate from China Clay**—White Sulphate of Alumina—Properties of Aluminium Sulphate—Use of Bauxite, Alunite, and Cryolite in the Manufacture of Alum—Alunite, Alumstone—Manufacture of Alum from Bauxite or Kaolin—Properties of Potassium Alum—Ammonium Alum—Ammonium Iron Alum—Potassium Chrome Alum. **Some other Salts of Alumina**—Aluminium Acetate—Aluminium Chloride—Solid Sodium Aluminate—Technical Uses of Salts of Alumina—Mordants—Sizing Paper—Waterproofing and Fireproofing—Aluminium Soaps—Alum and Aluminium Sulphate. World Production of Bauxite—World Production of Aluminium—References - - - - - - - - - - - 49

SECTION LVI

THE ARTIFICIAL ZEOLITE OR PERMUTITE INDUSTRY

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

Literature—Manufacture—Removal of Calcium and Magnesium Salts from Water—Removal of Sodium and Potassium Salts from Water—Removal of Iron and Manganese from Water—Removal of Free Alkali from Water—Preparation of Salts of Different Bases by Exchange—Precipitation of Gold from Solution. Complete Exchange Zeolites—Carbonaceous Zeolites - - - - - - - 59

SECTION LVII

THE ARTIFICIAL GEM INDUSTRY

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

Literature—Composition of the Principal Precious Stones—Artificial Turquoises—Reconstituted Rubies—Genuine Rubies—White Sapphires—Blue Spinel—Blue Sapphires—Other Stones based on Corundum—Cultured Pearls—Imitation Diamonds—References - - - - - - - - - - - 63

SECTION LVIII

ALUMINOTHERMICS:
"Thermit" and its Applications

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.
Revised by WILFRID FRANCIS

PAGE

Literature—Uses of "Thermit" Slag—Technological Preparation of Metals and Alloys by the "Goldschmidt" Reaction—Uses of "Thermit" as a Heating Agent—Uses of "Thermit" as a Heating Agent and Source of Molten Steel—Use of "Thermit" Slag—Mode of Ignition—"Thermit" for Incendiary Bombs—"Thermit" for Demolition—Welding and Fabrication by "Thermit"—Modern Smelting Practice—Properties of Aluminium Powder—Ammonal—Production of Powdered Aluminium—Calcium and Magnesium by Reduction with Aluminium - 67

SECTION LIX

THE CALCAREOUS CEMENTS INDUSTRY

By ERNEST A. DANCASTER, B.Sc. (Lond.)
Revised by WILFRID FRANCIS

Literature—Nature and Composition of Lime and Cement. **Common Lime**—Properties and Manufacture—Marble—Limestone—Chalk—Other Sources of Lime—Lime Burning—Kilns. **Hydraulic Lime**—Chaux de Theil—Grappier Cements or Ciment Grapier—Scott's Selenitic Cement. **Puzzuolanic and Slag Cements**—Composition—Granulating the Slag—Drying the Slag—Ruggles-Coles Drier—Mixing and Grinding—Passow's Slag Cement—Snelus' Process of Preparing Cement—Iron Portland Cement—Puzzuolana. **Natural Cements**—Parker's Cement—Roman Cement—Medina Cement—Continental Natural Cements—American Natural Cements—Rosendale Cement—Louisville Cement. **Portland Cement**—First Made by Joseph Aspdin—Mixing the Raw Materials—The Wet Process—The Semi-Wet Process—Slurry Making Process—Vertical Slurry Mixing and Storing Tanks—Ram Pumps—The Dry Process—Crushing—Blake's Stonebreaker—Blake-Marsden "Frictionless Lever" Crusher—Wheeler Forced Feed Crusher—Hadfield's Gyratory Crusher—Roller Mill and Toothed Rolls—Capacity of Ball and Tube Mills—Grinding—Edge-Runners—Bar Disintegrators—Jeffrey Pulveriser—Abbé Ball Mill—Krupp Ball Mill—Kominor Mill—Molitor Ball and Ball-Tube Mill—Krupp's Pregrit Mill—Griffin Mill—Bradley Three-Roll Mill—Kent Mill—Maxecon Mill—Sturtevant Ring-Roller Mill—Armstrong-Vickers and Newell's Tube Mills—Compound Tube Mills—Dry Milling—President Dry Press—Eggett Moulding Machine—Burning to Clinkers. **The Rotary Kiln**—Construction—Bearings—Kiln Hood—Fuel—Dust Collectors—Beth Dust Collector—The Cooler—Smidth and Mosser Coolers—Shaking Coolers—Recuperators—Lurgi Cement Roasting Process—Lurgi Sinter Grate. **Stationary or Vertical Kilns**—Dome or Bottle Kiln—Johnson Kiln—Gibbons Kiln—Batchelor Kiln—Spackman's Kiln—Hoffman Ring Kiln—Continuous Stationary Kilns—Shaft Kilns—Stage Kilns—Dietzsch Kiln—Aalborg Kiln—Schneider Havenschild and Hotop Kilns—Storing and Grinding the Clinker—Storing and Packing the Finished Cement—Weighing Machines—Composition of Portland Cement—Magnesia in Cement—Analyses of Portland Cement—Various Formulæ—High Alumina Cement—Ciment Fondu—Hydration of Cements—Heat of Hydration of Cements—Adulteration of Portland Cement—Action of Sea Water on Portland Cement—Types of Portland Cement—White Portland Cement—Super Cements—Sand Cement. **The Plaster Cements**—Prepared from Gypsum—Processes Employed in Manufacture—Plaster of Paris and the Cement Plasters—Calcining

SECTION LXIII

LUTES AND MISCELLANEOUS CEMENTS

By Geoffrey Martin, D.Sc., Ph.D.

PAGE

Literature—Cements to Resist Nitric and Sulphuric Acid—Lute Proof against Nitric and Hydrochloric Acid Vapours—Lutes for Chemical Retorts—Crucible Lutes—Crucible Cements—Cement for Furnaces—Cement to Resist White Heat—Water-glass, Zinc, and Pyrolusite Cement—A Joint which will Resist Great Heat—Non-conducting Cements for Covering Boilers and Steam-Pipes—Cement for Fixing Tiles into Fireplaces and Grates—Cement for Fixing Iron Bars into Stone—Cements for Seams and Joints of Stone Cisterns—Cement for Steam and Water Joints—Cement for Cisterns and Water Courses—Rust Iron Cement for Cast-Iron Cisterns—Enamel Glaze Cement for Coating Iron Pans—Cement for Marble—Keene's Marble Cement—Cements for Joining Metals and Wood—Cements for Joining Metals to Earthenware—Cements for Joining Metals to Glass—Turner's Cement—Cement for Plumbers—Cement for Joining Porcelain Heads to Metal Bars—Compositions Insoluble in Benzene and Petroleum—Joints which will Resist Benzene—Lute for Neck of Bottles with Glass Stoppers—Dental Cements—Refractory Cements—Acid-proof Cements - - - - - 146

SECTION LXIV

CLAYS AND ALLIED MATERIALS

By Alfred B. Searle

Literature—Occurrence—Chemical Constitution—Plasticity—Shrinkage—Impurities—Flux—Limestone—Sand—Metallic Oxides and Silicates. **Clays of Commercial Importance**—Adobe Clay—Alluvial Clay—Alum Shales—Ball Clays—Boulder Clays—Brick Clays and Brick Earths—Cement Clays—Marl China Clay or Kaolin—Crucible Clays—Fireclays—Fuller's Earth—Ganister—Grog—Kaolinite—Loams—Pipeclay—Puddling Clay—Red-Burning Clays—Rubbers—Refractory Clays—Saggar Clays—Shales—Oil Shales—Alum Shales—Slates—Sails—Surface Clays—Tender Clays—Vitrifiable Clays—Yellow or Buff-Burning Clays. **Analysis of Clays**—Physical Tests - - - - - - - - - - - - - 149

SECTION LXV

POTTERY

By Alfred B. Searle

Revised by Marcus Francis

Literature—Importance—The Classification of Pottery—Porous Pottery—Non-Porous Pottery—Unglazed Pottery—Terra-Cotta—Faience—Chinaware and Porcelain—Various Kinds of Porcelain—Stoneware—Physical Properties of Pottery—Strength of Pottery Bodies—Manufacture of Pottery—Statistics—References - - - 161

PAGE

SECTION LIX—*continued.*

in Kilns—The Dumesnil Kiln—Rotary Kilns—Mannheim Calciner—Cummer Rotary Calciner—Calcining in Kettles—Grinding—Retarders and Accelerators—Hardening Plaster—Flooring Plasters—Hard Finish Plasters—Keene's Cement—Mack's Cement—Parian Cement. **Mortar, Concrete, Plaster, and Stucco**—Mortars—Cement Mortar—Concrete—Armoured or Reinforced Concrete—Plasters—Stucco—Staff. **Waterproofing Cement Mortar and Concrete**—Sylvester and Meyer Processes—Fluates—Surface Hardening—Action of Calcium Chloride. **Chemical Analysis of Limes and Cements**—Common and Hydraulic Limes—Portland Cement—Metal Oxides—Sulphate—Sulphide—Alkalis—Insoluble Residue—Other Cements. **Physical and Mechanical Tests**—Specific Gravity—Fineness—Tensile Strength—Avery Testing Machine—Crushing Strength—Setting Time—Constancy of Volume and Soundness—Faija Test—Le Chatelier Test—Expansion—High Alumina Cements—Setting Time—Fineness—Soundness—Strength—Specific Gravity—Refractory Concrete. **Microscopic Examination**—Constituents found in Cement Clinker: Alite, Belite, Celite, Felite - - - - - - - - - - - - - - - 77

SECTION LX

SOREL CEMENT

By JAMES SHELTON, F.I.C.
Revised by WILFRID FRANCIS

Literature—Ingredients in Manufacture: Magnesite, Magnesium Chloride, and Carnallite—Magnesium Oxychloride—Artificial Marble—Other Uses—Zinc Oxychloride Cement - - - - - - - - - - - - - - - - - 137

SECTION LXI

ARTIFICIAL STONE

By JAMES SHELTON, F.I.C.

Literature—Process of Production—Concrete—Victoria Stone—Ward's Stone—Stuart's Granolithic Stone—Globe Granite—Non-Slip Stone—Clinker and Slag Blocks—Ford's Silicate of Lime Stone—Ransome's Artificial Stone—Plaster Cements—Marezzo Marble—Scagliola—Sorel Cement—Reconstructed Stone—Moreau Marble—Lime-Sand Bricks—Blast Furnace Slag—Reconstituted Stone—British Standard Specifications - - - - - - - - - - - 139

SECTION LXII

SODIUM SILICATE, WATER-GLASS, SOLUBLE GLASS

By JAMES SHELTON, F.I.C.
Revised by WILFRID FRANCIS

Literature—Methods of Manufacture—Alternative Methods of Production—Dissolving Silicate Glass—Properties and Uses—Silicates as Adhesives—Briquettes—Cements—Soaps—Metal Cleaning—Other Uses - - - - - - - - 142

SECTION LXVI

EARTHENWARE

By Alfred B. Searle
Revised by Marcus Francis

PAGE

Application of Term—Coarse Earthenware—Fine Earthenware—Calcareous Earthenware—Siliceous Earthenware—Constituents of Earthenware—Raw Materials—Fluxes or Glass-Forming Materials—Refractory Substances—Colouring Materials—Testing Raw Materials—Earthenware Bodies—Consistency—Methods of Shaping Ware — Modelling — Throwing — Turning — Moulding — Jolleying — Presses — Casting—Finishing—Slipping and Sticking Up—Engobing—Drying Earthenware—Shrinkage—Ovens. **Setting or Placing**—Firing—Trials—Glazes—Fritting—Mixture of Frits—Mixture for Glaze. **The Decoration of Earthenware**—Underglaze Painting—Overglaze Decoration—Tunnel Kilns—Decorating Kiln—Muffled Kiln—Probable Future Progress - - - - - - - - 167

SECTION LXVII

PORCELAIN

By Alfred B. Searle
Revised by Marcus Francis

Literature—Varieties of Porcelain—Raw Materials—Felspar—Cornish or China Stone—Quartz — Steatite — Chalk — Magnesite — Grog — Bone Ash — Porcelain Bodies—Glazes—Glassy Porcelains—Parian Ware—Belech Porcelain—Chinese and Japanese Porcelains—Preparation of Porcelain Bodies. **Processes of Manufacture**—Moulding, Throwing, and Casting—Firing—Decoration—Underglaze—Overglaze—Cracked Ware—Crystalline Glazes—Matt Glazes—Flowing Glazes—Rouge Flambé—Lustre Glazes. **ELECTRICAL PORCELAIN**—Literature—Nature—Steatite Bodies—Cordierite Bodies—Condenser Bodies—Zircon Porcelain—Spark Plug Bodies—Making Methods—Plug Performance Figures. **DENTAL PORCELAIN**—Literature—Manufacture - - - - - - - - - 195

SECTION LXVIII

STONEWARE AND SANITARY WARE

By Alfred B. Searle

Literature—The Term "Stoneware"—Sanitary Ware—Fine Stoneware—Glazes—White Ware—Casting—Chemical and Culinary Stoneware—Drain Pipes—Glazed Pipes—Paving Blocks and Tiles—Testing—References - - - - 207

SECTION LXIX

BRICKS

By Alfred B. Searle

PAGE

Literature—Groups—Building Bricks—Facing Bricks—Common or Stock Bricks—Variations in Crushing Strength—Engineering Bricks—Refractory or Furnace Bricks—Paving Bricks—Glazed Bricks—Sand-Lime Bricks—Raw Materials—Impurities—Red Bricks—White Bricks—Buff Bricks—Preparation of Material—Diesel-driven Excavator—Dragline Excavator—Cleaning Plant—Wash Mill—Crushing Rolls—Edge-Runner Mills—Tempering—Moulding—Expressing—Wire-Cut Process—Stiff Plastic Process—Semi-Dry Process—Drying—Burning—Kilns—"Clamp" Kiln—Archless Kiln—Single Kilns—Up-Draught Kilns—Down-Draught Kilns—Horizontal Kilns—Semi-Continuous Kilns—Hoffman Kiln—Staffordshire Kiln—Tunnel Kilns—De-airing—Testing—Future Progress - 213

SECTION LXX

SAND-LIME BRICKS

By Alfred B. Searle

Literature—The Mixture for Sand-Lime Bricks—Specifications - - - - - - 239

SECTION LXXI

TILES AND TERRA-COTTA

By Alfred B. Searle

Literature—Tiles—Roofing Tiles—Paving Tiles—Glazed Tiles. Architectural Terra-Cotta—Hollow Partition Blocks—Flooring Blocks - - - 241

SECTION LXXII

FURNACE LININGS AND OTHER REFRACTORY MATERIALS

By Alfred B. Searle

Literature—Raw Materials—Bricks for Gas Retorts—Glassmakers' Pots and Crucibles—Kilns—Silica Bricks—Dinas Bricks—Neutral Bricks—Chromite Bricks—Bauxite Bricks—Chrome Magnesite Bricks—Carbon Blocks—Insulating Bricks—Silicon Carbide Bricks—Refractory Cements—Future Progress 245

SECTION LXXIII

GLASS

By Alfred B. Searle
Revised by Marcus Francis

PAGE

Literature—Description of Glasses—Commercial Importance of Glass Industry—Normal Glasses—Chemical Constitution of Glasses—Formulæ—Structure of Glass—Devitrification—Glass "Stones"—Blisters or Seeds—Silicate Phase Diagram—Rate of Crystal Growth—Temperature/Viscosity Curves—Annealing Temperatures—Melting Points of Glass Types—Properties of Glasses—Spun Glass—Composition of Glass Types—Chemical Properties of Glass—Physical Properties. **The Raw Materials used for Glass-Making**—Silica—Soda—Sodium Carbonate—Potash—Lime—Magnesia—Zinc Oxide—Boracic Acid—Phosphoric Acid—Arsenic and Antimonic Acids—Barium Oxide—Alumina—Lead Oxide—Cullet—Decolorants—Red Lead and Nitre—Nickel Compounds—Selenium Compounds—Colouring Agents. **Technical Classification of Glasses**—Crown Glasses—Bohemian Glasses—Flint Glasses—Bottle Glasses—Boro-Silicate Crown Glasses—Boro-Silicate Flint Glasses—Phosphate Glasses—Silica-Free Glasses—Water-Glass—Opaque and Coloured Glasses—Hollow Ware—Bottle Glass—Bead Glass. **Mixing and Preparing the Glass**—Proportions—Loss in Form of Scum—Various Recipes. **Glass-Working**—Methods Employed—Blowing—Casting—Rolling—Pressing—The Brühler Machine—Making of Plate or Sheet Glass—Drawn Sheet Glass—Libbey-Owens Machine—Fourcault Process—Sievert's Process—Crown Sheet—Fluted Sheet—Defects in Glass—Casting of Glass—Reinforced Glass—Figured Plate—Pressing—Annealing—Hardened Glass—Bending or Cutting—Ground Glass—Engraving—Cameos—Etching and Embossing—Frosting—Iridescent Glass. Light Bulbs—Hollow-ware—Pressed Ware. **Optical Glass**—Production and Working of Optical Glass—Qualities Desired in Optical Glasses—Manufacture. **Special Glasses**—For Chemical Purposes—Steam Boiler Gauges—Lamp and Gas-Burner Chimneys—Transparent to Selected Rays—Electrical Insulation—Thermometers—Artificial Gems—Composition of Special Purpose Glasses. **Defects in Glasses**—Decay—Defects: Glasses which have been Badly Manipulated—Glasses which have Decayed by Exposure to Unsuitable Conditions—Glasses of Defective Composition. **Opaque and Coloured Glasses**—Porpora Glass—Copper Ruby Glass—Aventurine Glass—Methods of Colouring Glass—Green Glass—Blue Glass—Violet Glass—Brown Glass—Yellow Glass—Black Glass—Pinkish Shades—Red Glass—Silver Stain—White Opaque Glass—Gilded Glass—Modern Views on the Constitution of Glass—References. **Quartz Glass or Fused Silica Glass**—Literature—Composition of Fused Silica—Shenstone's Process—Heræus Process—Vitreosil—Thermal Syndicate—Voleker's Process—Properties of Fused Silica—Optical Quartz Glass—References - - - - - - - - - - - - - - 253

SECTION LXXIV

ENAMELS

By Alfred B. Searle
Revised by Marcus Francis

Literature—Use of Term—Vegetable Enamels—Paint Enamels—Glassy Enamels—Glazes—True Enamels—Dangers in Use of Enamelled Ware—Types of Ware—Mode of Manufacture—Materials Used in Enamelling—Ground Coats—Art Enamels—Recent Developments—Production Capacities of Enamelling Furnaces—Process Control - - - - - - - - - - - - 305

SECTION LXXV

THE ASBESTOS INDUSTRY

By Wilfrid Francis

PAGE

Literature—Definition. **Amphibole Asbestos**—Tremolite—Actinolite—Anthophylite—Amosite—Crocidolite. **Serpentine Asbestos**—Occurrence—World Production—Preparation—Properties. **Uses of Asbestos**—Asbestos Textiles—Packing Materials—Resin-bonded Products—Thermal Insulating Compositions—Asbestos Paper and Millboard—Asbestos Cement—Grading and Classification—Health Hazards—References - - - - - - - - - - - 313

SECTION LXXVI

THE MICA INDUSTRY

By F. W. Penny, B.Sc., F.G.S.
Revised by Wilfrid Francis

Literature—Occurrence—Species of Mica: Muscovite—Phlogopite—Lepidolite—Biotite—Manufacture—Uses—Phlogopite—Shell-Mica Production—Types—Statistics—Value—Vermiculite—Synthetic Mica - - - - - - - - - - - 321

SECTION LXXVII

THE THORIUM AND CERIUM INDUSTRY

By Norbert Berkowitz

Part I. Thorium.

Literature—Occurrence—Monazite Sand—Thorianite and Thorite—Analyses of Thorite and Orangite—Thorianite—Concentration of Monazite Sand—Extraction of Thorium—Purification of Thoria—Preparation of Metallic Thorium—Solubilities of Thorium and other Sulphates—Solubilities of Rare Earth Oxalates—Analysis of Thorium Minerals—Physical Properties of Thorium. **Incandescent Gas Mantle Industry**—Effect of Ceria on Emissivity of Thoria—Preparation of Fabric—Testing Thorium Nitrate for Mantle Manufacture. **Occurrence of Radio-active Thorium Minerals** - - - - - - - - - - 327

Part II. Cerium.

Literature—Occurrence—Cost of Cerium—Separation from Associated Oxides—Metallic Cerium—Cerium in Industry—Pyrophoric Alloys Industry—Other Uses for Cerium—Estimation of Cerium—References - - - - - - - 342

SECTION LXXVIII

TITANIUM

By Norbert Berkowitz

Literature—Occurrence—Geographical Distribution of Titanium Ores—Preparation of Metallic Titanium—Properties of Titanium—Industrial Utilisation of Titanium—Analysis of Titanium Ores—Prices—References - - - - 347

SECTION LXXIX

ZIRCONIUM

By Norbert Berkowitz

PAGE
Literature—Occurrence—Geographical Distribution—Extraction of Metallic Zirconium—Industrial Utilisation—Minor Uses—Analyses of Typical Zirconium Minerals—Methods of Analysis—References - - - - - - - - - - 355

SECTION LXXX

TANTALUM AND NIOBIUM

By Norbert Berkowitz

Literature—Occurrence of **Tantalum Minerals**—Geographical Distribution—Manufacture and Properties of Metallic Tantalum—Uses of Metallic Tantalum—Estimation of Tantalum and Niobium in Minerals - - - - - - 361
Occurrence of **Niobium (Columbium)**—Uses—Prices—Estimation in Niobium-Chrome Steels—References - - - - - - - - - - 365

SECTION LXXXI

TUNGSTEN

By Norbert Berkowitz

Literature—Occurrence—Geographical Distribution of Tungsten Ores—Extraction of Tungsten from its Ores—Properties of Metallic Tungsten—Tungsten in Industry—Tungsten Carbide—Prices—Analysis of Tungsten Ores - - - - - 367

SECTION LXXXII

THE ELECTRIC LAMP INDUSTRY

By Sydney J. Johnstone, B.Sc.
Revised by Wilfrid Francis

Literature—Manufacture of Carbon Filament Lamps—Metallic Filament Lamps—The Tantalum Lamp—The Tungsten Lamp—Process of Making Tungsten Filaments—Colloidal Tungsten Filaments—Drawn Wire Filaments—Manufacture of the Lamp—Vacuum Lamps—Gas-filled Lamps—Lamp Ratings and Efficiencies—Fluorescent Lighting—Cold Cathode Tubes—Hot Cathode Tubes - - - 373

SECTION LXXXIII

URANIUM

By Norbert Berkowitz

PAGE

Literature—Natural Occurrence—Geographical Distribution of Uranium Ores—Manufacture of Metallic Uranium—Treatment of Ores—Reduction of Ores—Utilisation of Uranium—Occurrence of Radioactive Ores - - - - - - - 357

SECTION LXXXIV

VANADIUM

By Norbert Berkowitz

Literature—Natural Occurrence—Extraction Processes—Acid Extraction Processes—Alkaline Extraction Processes—Properties of Metallic Vanadium—Vanadium in Industry—Analysis of Vanadium Ores and Alloys - - - - - - - 393

SECTION LXXXV

THE INDUSTRY OF RADIOACTIVE SUBSTANCES

By Norbert Berkowitz

Literature—Introduction—Nature of Radioactive Emissions—Theory of Radioactivity—Radioactive Constants—Position of Radio-elements in Periodic Table—The Radioactive Series—Induced Radioactivity—Measurement of Radioactive Intensity—Proportional Amplifier. **Separation of Radio-elements—Chemical Methods**—Radium—Ionium—Polonium—Mesothorium—Radiothorium. **Separation of Isotopes**—Physical Methods—Uses of Radioactive Substances—Occurrence of Radioactive Ores - - - - - - - - - - 399

SECTION LXXXVI

ELECTRIC FURNACE PRODUCTS INDUSTRY

By H. D. K. Drew, B.Sc. (Lond.)

Revised by Wilfrid Francis

Literature—**Silicon Carbide**—Carborundum—Manufacture—Properties—Uses of Carborundum—Statistics—Silundum Articles—Siloxicon—Monox. **Manufactured Graphite**—Occurrence and Mode of Formation—Graphite Powder—Uses—The Graphitising of Electrodes. **Alundum**—Silicon—Properties. **Ferro-Silicon**—[illegible]. **Calcium Carbide**—Raw Materials—Electric Furnaces Used—Properties and Uses—Acetylene Gas—Calcium Cyanamide—Nitrolim—Statistics. **Modern Electrothermal Processes**—Reduction of Phosphorous—Production of Pig-iron—Reduction of Aluminium and Chrome—Powder Metallurgy—References - 413

SECTION LXXXVII

GRINDING AND POLISHING MATERIALS

By Alfred B. Searle

PAGE

Literature—Abrasive Nature of Grinding Materials—Hard Mineral Abrasives—Mild Mineral Abrasives—Waxy Polishes—Mill Stones—Grinding Wheel—Sizes of Grain in the Abrasive—Table giving Grade and Grain for Different Classes of Work—Hard Abrasive Powders—Diamonds—Carborundum—Corundum—Corubin—Emery—Electrite—Sand—Crushed Steel—Chalk—Lime—Rouge—Tripoli Powder or Rotten Stone—Kieselguhr—Pumice Stone—Polishes—Metal Polishes—Furniture Polishes—French Polish—Boot and Shoe Polishes—Boot Blackings—Stove Polishes—Mechanical Methods of Polishing - - - - - 433

SECTION LXXXVIII

PHOSPHORUS

By C. Ainsworth Mitchell, B.A. (Oxon.), F.I.C.
Revised by Wilfrid Francis

History—Process of Manufacture—Readman and Parker's Process—Neumann's Process—Harding's Process—Recent Developments in Production and Uses—Properties—Allotropic Modifications of Phosphorus—Red Phosphorus—Hittorf's Violet Phosphorus—Pyromorphic Phosphorus—Schenk's Scarlet Phosphorus—Totenhaupt Modification—Bridgman's Black Phosphorus—Colloidal Phosphorus—Uses—Calcium Phosphide—References - - - - - - - - - 443

SECTION LXXXIX

MATCHES

By C. Ainsworth Mitchell, B.A. (Oxon.), F.I.C.
Revised by Wilfrid Francis

Literature—"Friction Lights"—"Lucifer" Matches—Typical Specimens of Early Matches—Early Phosphorus Matches—First Safety Matches—Composition of White Phosphorus Matches—Safety Match Compositions—Ichtenhäuser's Formula—After-Glowing—Prohibition of White Phosphorus Matches—"Double-Dip" Matches—Substitutes for White Phosphorus. Use of Phosphorus Sulphides—French State Matches—Match Manufacture - - - - - - - 451

SECTION XC

ATOMIC POWER

By Norbert Berkowitz

Literature—Conversion of U-238 to Plutonium—Principle of Atomic Power "Piles"—Neutron Moderators—Resonance Capture—Neutron Reproduction—Divergent Chain Reaction—Health Hazards—Future Developments - - - - - 455

INDUSTRIAL & MANUFACTURING CHEMISTRY

(INORGANIC)

SECTION LII

DISINFECTANTS, ANTISEPTICS AND ANTIBIOTICS

By Geoffrey Martin, D.Sc., Ph.D.

Revised by Wilfrid Francis

LITERATURE

M. Christian.—"Disinfection and Disinfectants." London, 1931.
American Public Health Association.—"Chlorination in Sewage Treatment." 1934.
R. R. Mullen *et. al.*—"Sulphanilamide Therapy of Bacterial Infections." Springfield, Illinois.
Annual Reports on the Progress of Applied Science, Soc. Chem. Ind., London.-
T. S. G. Jones *et. al.*—Conference on Antibiotics, N.Y. Acad. Sci., May 1948.
B.I.O.S.—Final Rept., 1404, Items 22–24, 225.
See also references in the text and on pages 16*a* and 16*b*.

Disinfectants are germicides; that is to say, they kill bacteria and other lowly organisms which injuriously affect the upper forms of life.

After disinfection usually there remains a residue of harmless, highly resistant organisms, which often act beneficially by consuming injurious organic matter and organisms. In practice a complete annihilation of all organisms would be difficult to attain economically.

Antiseptics are less powerful than disinfectants in that they only retard or prevent the growth of injurious lower organisms in suitable media.

The **germicidal power** and the **antiseptic power** of a material are not always simply related. For example, guaiacol has only 0.9 the germicidal value of phenol, whereas it is two and a half times as effective as an antiseptic, *e.g.*, it takes two and a half times as much phenol as guaiacol to stop an organism **developing** in a broth (antiseptic action), whereas when it comes to killing an already existing organism 0.9 part of phenol has the same action as 1 part of guaiacol (germicidal action).

Antibiotics are substances derived from moulds and other micro-organisms and capable of destroying specific viruses, bacilli, bacteria, and cocci.

Testing Disinfectants.—The tests usually employed for comparing the germicidal action of disinfectants are the Rideal-Walker test (B.S. 541, 1934) and the Chick-Martin test (B.S. 808, 1938).

For further details of the methods of carrying out these tests see B.S. 541 and 808.

In the Rideal-Walker test the standard disinfectant is pure **phenol** (carbolic acid), C_6H_5OH, and the power of a disinfectant is expressed numerically in multiples of the amount of pure phenol which will achieve the same germicidal result. This multiple is called "**the Rideal-Walker carbolic acid coefficient,**" or "**germicidal value**" of the disinfectant.

PART I.—ORGANIC DISINFECTANTS AND ANTISEPTICS

Coal Tar Fluids.—These consist of dark, thick fluids, smelling of coal tar, and containing phenolic bodies or their sodium or potassium salts mixed with soaps, resins, etc.

Water Soluble Solutions are achieved by converting the phenols into their sodium or potassium salts.

For example, a well-known mixture consists of crude creosol, 1 part; potassium soap, 1 part; which are heated together with stirring; often alcohol or glycerol is added to such mixtures to increase the solubility in water.

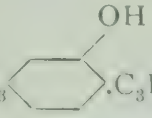
Recently linseed and other oils have been sulphonated, cresylic acids then mixed into the liquid, and caustic soda or potash added in sufficient amount to obtain a water-soluble neutral solution.

The liquids which yield **emulsions** with water consist of nearly insoluble cresylic and other phenolic acids, mixed with soaps, resins, oils, gelatine and soda.

The cresylic acids and similar homologues of phenol are much less soluble and much less poisonous to man than free phenol, and at the same time have a higher germicidal value. Consequently, most of the commercial coal tar disinfectant fluids are now practically free from phenol, and are practically non-poisonous. The Privy Council Orders of 1900 and 1902 prohibit the uncontrolled sale of liquors containing more than 3 per cent. phenol or its homologues.

Guaiacol (methyl-catechol, $C_6H_4(OH)(OCH_3)$) and **creosol** (methyl guaiacol, $C_6H_4(OCH_3)_2$) are contained in wood creosotes, and form the basis of disinfectants and antiseptics much used in the treatment of tuberculosis.

The germicidal value (Rideal-Walker coefficient) of guaiacol is only 0.9 that of phenol, whereas its antiseptic power (*i.e.*, power of preventing the growth of bacteria) is stated to be 2.5 times that of phenol. A 1 per cent. solution kills *B. tuberculosis* in two hours.

Thymol (CH_3$.C_3H_7$), present in oil of thyme, in saturated solution (0.3 per cent.) arrests putrefaction.

Resorcinol (m-dihydroxybenzene, m-$C_6H_4(OH)_2$), **catechol** (o-dihydroxybenzene, o-$C_6H_4(OH_2)$) and **hydroquinone** (**quinol**, p-dihydroxybenzene, p-$C_6H_4(OH)_2$) and **pyrogallol**, $C_6H_3(OH)_3$, are all powerful medicinal antiseptics.

A 1 per cent. solution of resorcinol is very effective. A 9 per cent. solution is sold as "Andeer's lotion." Bismuth iodo-resorcin sulphonate is sold under the name of "anusol."

Pyrogallol ($C_6H_4(OH)_3$) is an effective bactericide in a 3 per cent. solution. It is, however, poisonous and quickly oxidises.

The antiseptic values of these phenols may be taken as hydroquinone 30, resorcinol 25, catechol 20, pyrogallol 15, phenol being taken as 20.

The Rideal-Walker carbolic acid coefficient of **resorcinol** is 0.30, of **catechol** is 0.25, and of **pyrogallol** is 0.22.

Beta-naphthol ($C_{10}H_7(OH)$) is much used for internal disinfection, the usual dose being 3-10 grains.

A solution of 0.5-1.0 per cent. of B.-naphthol dissolved in alkaline carbonate solution kills typhoid germs in a short time. The free B.-naphthol has a greater germicidal action than its alkaline salts.

B.-naphthol, up to 10-15 per cent., is much used in ointments in certain skin diseases. Certain derivatives of B.-naphthol are very powerful disinfectants. Among these may be mentioned the non-poisonous and odourless **halogen substituted naphthols**. For example, **tribromonaphthol** ($C_{10}H_4Br_3(OH)$) in dilutions of 1 : 250,000 has a decided germicidal action.

The halogen substituted naphthols are, next to mercuric chloride, the most powerful disinfectants.

The easily soluble **calcium or aluminium salts** of **B.-naphthol sulphonate** are in the market under such names as "abrastol," "alumnol," etc.

A dilution of 1 : 250 will inhibit the growth of pus cocci and similar bacteria.

Various essential oils have a distinct antiseptic value. **Oil of eucalyptus** (Rideal-Walker coefficient 1.2) and **pinol** are widely used. **Sanitas** owes its disinfecting powers to the slow oxidation of certain essential oils, whereby **ozone** is generated, reabsorbed, and the oil regenerated.

Benzoic acid ($C_6H_5.COOH$), and salts thereof, are powerful antiseptics. 1 part dissolved in 400 of water kills *B. typhosus* in three or four minutes, 0.022 per cent. benzoic acid in milk retards souring, 0.26 per cent. sodium benzoate and 0.29 per cent. potassium benzoate having an equal value. Rideal-Walker coefficient is 5.0.

Benzoic acid and benzoates are not poisonous, 0.5 grain per day in food leaving no injurious effect on man. Hence the use of benzoic acid and benzoates in food-preservation; their taste and smell, however, tend to flavour the goods.

Salicylic acid ($O - C_6H_4(OH).COOH$) is widely used as an antiseptic. It is only sparingly soluble in water (1 : 500), and at this dilution it takes three hours to kill *B. typhosus.*

Its food-preservative value is about that of benzoic acid. Moulds and ferments are inhibited by 0.1 per cent., smaller quantities than this being inefficient.

Salol (phenyl-salicylate, $C_6H_4.OH.COOC_6H_5$) is used as an internal antiseptic, being hydrolysed when in the intestines into phenol and salicylic acid.

Salophen is p-aminophenyl acetyl salicylate; it has a stronger antiseptic action than salol.

Acetic acid, propionic acid, tartaric and citric acid have all a distinct preservative power towards certain bacteria.

A 5 per cent. solution of **acetic acid** was found by Rideal to kill *B. coli* in five minutes; a 2.5 per cent. solution killed it in fifteen minutes, while the bacteria were unaffected after forty minutes by 0.5 per cent. solution. The Rideal-Walker coefficient for acetic acid is 0.6. Cholera germs are stated to be killed by 0.08 per cent. solutions of **citric acid**, and typhoid germs by 0.1 per cent.

Citric and **tartaric** acid solutions, however, soon go mouldy in warm weather.

Lactic acid has considerable disinfecting and germicidal value, having a Rideal-Walker coefficient of 1.8. It is much used in various fermentation industries as an antiseptic.

Formic acid ($HCOOH$) is a powerful antiseptic and germicide, the Rideal-Walker coefficient being 5.7.

According to Rideal a 0.5 per cent. aqueous solution will kill *B. typhosus* in fifteen minutes, and 0.1 per cent. solution will kill this organism in thirty minutes, and will inhibit the growth of mould. Formic acid, however, is less efficient than formaldehyde in destroying spores. The salts of formic acid are not effective disinfectants.

Formaldehyde ($H.CHO$) is sold as an antiseptic as a 40 per cent. solution under the name "**formalin.**" The Rideal-Walker coefficient is 0.55. A solution of 1.5 per cent. formaldehyde (3 pints formalin in 10 galls. of water) will keep fruit immersed therein for ten minutes for ten to twenty-one days longer than when untreated. 1 part formaldehyde in 50,000 water (1 part formalin to 20,000 water) will keep milk from souring for twenty-four hours without injury to health. 1 part formalin to 10 parts water is used for preserving bodies for dissection, etc. 0.003–0.03 per cent. stops the development of bacteria; 0.007–0.060 stops the development of yeasts; while moulds are inhibited by 0.03–0.125 per cent. Soft potassium soaps impregnated with formalin are much used in operations for instrument and hand disinfection.

Formaldehyde in small amount is present in smoked fish and bacon (1 : 10,000 to 1 : 100,000 of weight of goods) and is one of the agents which effect preservation of smoked provisions.

Paraformaldehyde, paraform, triformal $(CH_2O)_3$, is a solid polymer of formaldehyde. It dissociates when heated into gaseous formaldehyde. It is only slightly soluble in water. It is used for disinfecting instruments, also as an internal disinfectant. It is also widely used as a means of generating gaseous formaldehyde for disinfecting rooms, etc.

Hexamethylene tetramine ($C_6H_{12}N_4$), made by evaporating together ammonia and formaldehyde, forms the basis of a large number of antiseptic preparations.

Iodine cyanide (ICN) is fatal to all lower forms of life, and its use as a preservative for biological specimens has been suggested by Kobert.

Iodoform (CHI_3) is a powerful antiseptic, formerly much used in surgery, although it is stated to be less efficient than a dilute solution of iodine.

Carbon tetrachloride (CCl_4) kills typhoid germs, but **chloroform** ($CHCl_3$) vapour does not, although the latter is efficient in aqueous solutions (0.62 per cent. solution takes thirty minutes), and chloroform is frequently employed for preserving specimens and infusions.

Other Organic Substitution Compounds of Chlorine, Bromine, and Iodine.—Most of these have a high antiseptic value.

Organic Dyes.—Many organic dyes possess a marked, and sometimes specific, germicidal action. They may, therefore, be used as non-irritant and painless antiseptics. **Acriflavine** is one of the best known, either in aqueous solution, or normal saline, or as an emulsion with the addition of tannic acid. This emulsion is extremely effective for the treatment of burns and scalds. Acriflavine, or trypaflavine, is 2 : 8 diamino 10-methylacridinium chloride. In addition to its use as an antiseptic, acriflavine is also used in the treatment of sleeping sickness. Another dye of the phthalein series, and at one time popular in the U.S.A. as a wound dressing, is mercurochrome. This dye is also used in the treatment of infections of the genito-urinary tract. Nile blue, one of the oxazine series of dyes, will kill protozoa in extremely dilute solutions without killing bacteria, and it has therefore been suggested for the destruction of protozoa in sewage in the activated sludge process, which depends upon bacteria for its successful operation.

Halogenated Phenolics. The addition of halogens to phenolic compounds increases their germicidal activity, and a number of antiseptic solutions have recently been developed on this principle. Amongst these are **Dettol**, which is a halogenated xylenol in a solution of saponified oils of the terpene series, and **T.C.P.** which is a dilute solution of chlorinated and iodised phenol and salicylic acid. Both are non-irritant and painless antiseptics.

PART II.—INORGANIC DISINFECTANTS

Oxidising Disinfectants

Ordinary oxygen (O_2) has a distinct germicidal value, especially in the presence of light. Its active modification, **ozone** (O_3), is one of the most powerful disinfectants known.

According to Rideal, ozone in the proportion of 0.6 g. per cubic metre of water (*i.e.*, 6 lbs. per 1,000,000 galls.) destroys all dangerous bacteria in average filtered river water.

Ozone treatment effects a great improvement in the physical and chemical properties of the treated water, and leaves no injurious chemicals behind in the water.

Ozone treatment can only be applied to **clean** filtered water, *i.e.*, water free from much oxidisable matter, ferrous salts, etc., otherwise the consumption of ozone would be too great, this substance being rapidly destroyed by organic and oxidisable matter.

Ozone has also been used for improving the air of underground railways and the like.

Ozone is especially active towards micro-organisms when **moist**, less so when **dry**.

Ozone is absorbed by certain essential oils and confers on them oxidising and disinfecting properties. This is the basis of the well known disinfectant "**Sanitas**".

Various other liquids absorb **ozone** and the resulting fluids are powerful oxidising agents. Thus, **acetaldehyde** absorbs 2,800 vols. of ozone; a 10 per cent. solution of acetaldehyde in water absorbs 536 vols. of ozone.

Alcohol is stated to absorb 750 vols. and **ether** 800 vols., forming stable solutions which can be used in surgery for sterilising purposes.

It should be noted that many ozonides are explosive.

For further details regarding the use of ozone as a disinfectant see this work, Vol. I., under **Ozone** and also under **Water**.

Hydrogen peroxide (H_2O_2) is a powerful germicide. In dilute solution it does not injure foods, and is non-poisonous. It does not destroy enzymes such as **diastase**, **pepsin**, **pancreatin**, **ptyalin**, although it attacks and destroys certain other enzymes, such as **catalase** (contained in malt, milk, yeast, etc.).

These properties make hydrogen peroxide very suitable as a preservative for milk and similar foods. Rideal states that when milk is treated with 0.6 g. H_2O_2 per litre and heated to 52°-56° C. for eight hours, the milk kept unchanged for four weeks in a closed receptacle, and was unchanged in physical properties. Thus the pasteurisation of milk is effected at a lower temperature in the presence of hydrogen peroxide.

One per cent. of hydrogen peroxide will destroy pathogenic bacteria in about twenty-four hours.

Hydrogen peroxide is largely used as a spray, gargle, and a dressing for wounds; also as an internal disinfectant.

It is sold under various names, such as **perhydrol** (30 per cent. solution giving off 100 vols. of oxygen); **dioxogen** (3 per cent.); "**peroxol**," "**pyrozone**," "**glycozone**"; all these contain hydrogen peroxide, sometimes mixed with other disinfectants.

A solution of hydrogen peroxide in ether, containing 1.2 per cent. H_2O_2, has been used in scarlet fever and whooping cough under the name "**ozonic ether**."

Ethereal solutions of hydrogen peroxide are more stable than aqueous solutions.

Metallic Peroxides

Foregger and Philipp observed that **calcium peroxide** is better than hydrogen peroxide for sterilising milk, the effects being much more durable.

For sterilising water tablets of **magnesium peroxide** and citric acid have been used.

The citric acid on coming into contact with the water attacks the magnesium peroxide, liberating hydrogen peroxide. According to Park 0.2 g. of magnesium peroxide killed 2,000,000 typhoid organisms contained in 150 c.c. of water in one minute. 0.1 g. magnesium peroxide achieved the same result in thirty minutes. Magnesium peroxide is the main constituent of "Hopogan." Calcium peroxide and magnesium peroxide have been advocated as a constituent of tooth powders.

Sodium peroxide also generates oxygen or hydrogen peroxide, and has disinfecting properties. Unfortunately it yields a strongly alkaline solution.

Zinc peroxide also evolves oxygen and has powerful antiseptic properties. It has been sold under the names "Dermogen" and "Ektogan."

Mercury peroxide has antiseptic properties, and has been used as a constituent of ointments and similar preparations.

Persulphates, **percarbonates**, and **perborates** have recently been introduced as disinfectants (see this work, Vol. I., under **Oxidising Agents**).

Permanganates and **manganates** have long been used as disinfectants under the name of Condy's Red and Green Fluids.

Both the sodium and potassium salts have powerful disinfecting properties, but the sodium salt seems to be preferred.

They owe their germicidal action to their oxidising properties, and are rapidly reduced by oxidisable matter, yielding brown oxide of manganese. Consequently disinfection by permanganates can only be economically exercised in cases where there is, comparatively speaking, only small amounts of oxidisable matter present. The Rideal-Walker coefficient of potassium permanganate is 42.

The usual method of application is to add the permanganate until the water remains permanently pink, and for polluted waters the pink colour should persist for twenty-four hours. This process of disinfection has long been practised in India in cases of water suspected of carrying cholera germs.

Chlorine and Hypochlorites

Chlorine, owing to its chemical properties, can act as a disinfectant by uniting with the hydrogen of water and liberating nascent oxygen, which then destroys the organisms. Chlorine also acts by directly attacking the organic matter, forming substituted compounds incapable of putrefying.

Chlorine acts as a direct poison towards bacteria. Chlorine water has a Rideal-Walker carbolic acid coefficient of 28.

Perhaps the most important disinfecting effect obtained by chlorine and by hypochlorites is an indirect one. The substitution compounds which they form with organic matter act themselves as powerful germicides.

Hypochlorites.—The Rideal-Walker coefficient of hypochlorites (calculated on "available chlorine") is 146–220. The chief hypochlorite used is "**chloride of lime**" or "**bleaching powder**" (calx chlorinata), which is prepared as described in this work, Vol. I., under **Bleaching Powder.** The active basis is **calcium hypochlorite.** Chloride of lime has the great advantage of being an easily transportable solid, and is very cheap; but it suffers from the serious disadvantages of being rapidly destroyed on exposure to moist air, takes a considerable time to pass into solution, and leaves behind a bulky residue of undissolved lime. Moreover, it leaves on the surfaces treated a layer of damp for a long time from the highly deliquescent calcium chloride. When applied for the purification of drinking water it imparts a bitter taste and increases its hardness. In spite of these disadvantages chloride of lime is very widely used for treating drinking water, especially in times of epidemics.

In Jersey City, U.S.A., 40,000,000 galls. of water per day are treated with 0.2 part of available chlorine (in form of chloride of lime) per million parts of water and the daily examination shows that *coli* is absent from 10 c.c. of the treated water.

At Antwerp 0.2 available chlorine per million is added to the storage reservoirs with a contact of twelve hours.

In disinfecting **sewages,** of course, a much larger amount of chloride of lime would be necessary. Instead of using pure chloride of lime, Duyck treats with 8 parts per million of ferric chloride and 0.5 part of chloride of lime. This clarifies the water. (Ferrochlore treatment.)

There is an increasing tendency to use **sodium hypochlorite** (for manufacture and properties see this work, Vol. I.).

Sodium hypochlorite solution is placed on the market as a disinfectant under several names.

Thus "**antiformin**" contains sodium hypochlorite and caustic soda, and has been much used in breweries. "**Chloros**" is a solution of sodium hypochlorite containing 10 per cent. available chlorine. "**Oxychloride**" contains 10–12 per cent. available chlorine. The old "**Eau de Javel**" was potassium hypochlorite (made by chlorinating potassium hydroxide). Its place is now taken by the well-known "**Eau de Labarraque**," which is a chlorinated soda containing 2.5 per cent. available chlorine.

"**Milton**" is a proprietory brand of sodium hypochlorite, prepared electrolytically, containing 1 per cent. of NaOCl and 6.5 per cent. of NaCl. It is stable and is much used in tropical countries.

Local disinfection can be achieved by sodium hypochlorite solutions containing 0.35 per cent. available chlorine, which will kill most organisms in a few minutes, and will destroy all pathogenic spores in the space of a couple of hours.

Clean filtered water, however, requires much less available chlorine to effect practical sterilisation. According to Rideal 0.75–1 part of available chlorine to each million parts of water destroys all harmful bacteria, and after the water has stood for a couple of hours its taste and odour are unchanged.

In the case of **sewage,** however, very much larger quantities of hypochlorite solution must be used in order to disinfect them. This is on account of the large amount of oxidisable matter. In fact, it is on this account uneconomical to directly disinfect sewage with hypochlorites. It is best to purify by other means (see disposal of sewage under **Water,** this work, Vol. I.), and finally use hypochlorite for imparting final sterilisation to the partially purified liquid.

In America it has been proved that treating sewage effluents with 2–5 parts per million of available chlorine applied as sodium hypochlorite will destroy about 97 per cent. of all bacteria in about two hours. Rideal states that 3 parts per million of available chlorine applied to partially purified effluents will reduce the bacterial contents to about 20 per 100 c.c. of liquid, while 17 parts per million of available chlorine completely destroyed all organisms in about fifteen minutes.

Raw sewage, however, required for complete sterilisation about 30–70 parts of available chlorine per million parts water, and a contact period of between four and five hours.

From these results it will be seen that time is an essential factor in causing efficient sterilisation. A small amount of disinfectant acting for several hours will cause almost complete sterilisation, whereas to achieve the same results in a few minutes requires a large proportion of disinfectant, and (except in the case of ozone and hydrogen peroxide) leaves behind in the treated water considerable amounts of residual chemicals, which affect the palatability and odour of the water.

The Break-Point Chlorination of Water.—In recent years it has become apparent that the amount of chlorine necessary to make drinking or bathing pool water safe depends upon the amount of residual chlorine available for oxidising impurities after reaction with ammonia or amines present in the water, and that the nature of the source of the chlorine added, whether this be chlorine gas or solutions or suspensions of hypochlorites, is of little importance. Indeed, the term chlorine stands equally for free chlorine, hypochlorous acid, or hypochlorite, since in solution the relationship between these alternative forms of chlorine depends primarily upon the pH value of the solution. When chlorine gas dissolves in water it is rapidly hydrolysed into hypochlorous acid and hydrochloric acid, according to the reversible equation:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

If alkali be added to such a solution, the reaction proceeds further in the direction from left to right and, within the range of pH from 3 to 6, hydrolysis is virtually complete and the whole of the available chlorine is present as hypochlorous acid. Above the pH of 6, the hypochlorous acid dissociates according to the equation:

$$HOCl \rightleftharpoons H+ + OCl-$$

The extent of the dissociation is also a function of pH and at pH = 9 the hypochlorous acid is completely dissociated. Within the range pH 6.5 to 8.0, the usual range of drinking and bathing pool waters, the percentage of undissociated hypochlorous acid falls markedly from about 90 per cent. to 20 per cent. In the control of waterworks and swimming baths, therefore, free chlorine means hypochlorous acid, whatever the mode of addition of the chlorine, and any analytical test for free residual chlorine measures the hypochlorite ion and the undissociated acid.

The presence of ammonia in solution complicates the problem, whether this be added, as in the ammonia-chlorine treatment of water, or whether it is present as pollution in swimming water, as ammonia or protein derivatives. If chlorine be added in increasing amounts to a water containing "free and saline" ammonia, the amount of residual chlorine first increases, then decreases until a "break-point" is reached, and then increases again, proportionally to the further additions of chlorine. According to Palin,(6) the first part of the curve corresponds to the formation of mono- and di-chloramines and the peak represents the point where all the ammonia initially present has been converted into these amines. In the presence of excess chlorine, the chloramines are unstable and react with the free chlorine, with diminution of the amount of available chlorine, until all the chloramines have been decomposed. According to Chapin(7) the relative amounts of mono- and di-chloramine formed at first are a function of pH, and their formation can be represented by the equations:

$$NH_3 + Cl_2 = HCl + NH_2Cl$$
$$NH_3 + 2Cl = 2HCl + NHCl_2$$

The ratios of chlorine to initial ammonia nitrogen corresponding to the peak of the curve vary from 5 : 1 to 10 : 1 according to the pH. The equations representing destruction of chloramines are:

$$NH_2Cl + NHCl_2 = N_2 + 3HCl$$
$$2NH_2Cl + Cl_2 = N_2 + 4HCl$$

These reactions are equivalent to the direct conversion of ammonia into nitrogen at the break-point, corresponding to a ratio of chlorine to ammonia of 7.6 to one, thus:

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$

In practice this means that chlorine is wasted if it is added after the first appearance of free chlorine, as distinct from residuals consisting of chloramines and similar compounds. Lower doses of chlorine than these give satisfactory bacteriological results, but to improve tastes and to remove odours it is necessary to go just beyond the break-point. By adopting this procedure minimal amounts of chlorine can be used and there is no necessity for treatment to remove excess of chlorine. Control of free chlorine is by the flash test, or the neutral test, both using ortho-tolidine as colorimetric reagent and devised by Laux.(8) In the first test, under acid conditions, the free chlorine is differentiated from the residual only because of the greater rate at which colour develops. In the second test, neutral ortho-tolidine is used, and in this case no colour is obtained before the break-point, but blue or yellow colours are developed immediately after the break. In a recent paper by Lea and Mills, the proper control of swimming bath waters may be effected by maintaining:

(1) Free residual chlorine at 1 to 2 ppm., with free residual chlorine in excess of combined residual chlorine.
(2) pH value at 7.2 to 8.0.
(3) Bicarbonate alkalinity at 200 ppm., expressed in terms of $CaCO_3$.

For further information on the subject see original papers in the literature, including a recent paper by Palin.(10)

Bromine and Iodine and their Derivatives

Bromine is an even more efficient germicide than chlorine, bromine water having a Rideal-Walker carbolic acid coefficient of 64 against 28 for chlorine water. The difficulty of using bromine extensively for sterilisation is the danger attending its use, although it is very efficient for rapid sterilisation in the field.

It has been suggested to use for sterilisation in the field free bromine in thin sealed glass tubes, and Rideal found that 20 parts per million of bromine sterilised *B. typhosus* in water in about thirty minutes. The process was employed in the Soudan campaign in 1898, using 60 parts of bromine per million of water with five minutes' contact, and removing the excess of bromine by 57 parts of sodium thiosulphate.

It has been disputed whether this process is efficient (see Schöder, *Zeitsch. f. Hyg.*, 1900, p. 53), and one objection is the formation of residual bromides.

"**Bromidine**" consists of a dry mixture of sodium bisulphate with sodium or potassium bromide and bromate. These react when moist to liberate free bromine. This material was introduced by Braithwaite. The main disadvantage is the entry of residual bromides into the drinking water.

Altmann's process consists in dissolving free bromine in potassium bromide solution. Forty parts of bromine with five minutes' contact per million parts of water sterilises the liquid. The excess of bromine is then removed by ammonia.

This process suffers from the defect that a bulky solution must be employed. Moreover, the expensive and physiologically active potassium bromide remains dissolved in the treated water.

Iodine.—Although free bromine is more rapidly absorbed by organic matter than free iodine, yet the latter appears to be a more vigorous poison towards protoplasm.

Cash proved that the quantities of chlorine, bromine, and iodine required for disinfection under similar conditions is nearly in the ratio of their atomic weights. The increase of toxicity with increase of atomic weight is apparent if we compare the germicidal value (Rideal-Walker coefficient) of chlorine water (28) with that of bromine water (64) and iodine water (100).

The high germicidal value of iodine makes it widely used as a constituent of ointments or tinctures in parasitic diseases. The surface of the skin is often disinfected before operations by painting with the tincture. Sometimes the surface of the skin is cleansed by applying a 1 per cent. solution in benzene or chloroform, especially prior to hypodermic injections.

Iodine has had a limited application for the purpose of sterilising water in the field. Thus, during the Thibet and Sikkim expeditions iodine tincture was applied to the water, the excess of free iodine being removed by the subsequent addition of sodium sulphite.

Nesfield's triple tablets, supplied for the purpose of sterilising water, consist of (1) a tablet of iodide and iodate, (2) a tablet of tartaric or citric acid. These are left in the water for two to three minutes, when the acid liberates free iodine from the iodate. Next, (3) a tablet containing sodium sulphite is added, which removes the free iodine. It is claimed that 4-5 parts of free iodine per million parts of water will destroy all typhoid, dysentery, and cholera germs.

Iodine trichloride (ICl_3) is used for sterilising the instruments and hands in surgical operations.

According to Rideal 50 parts ICl_3 per million of water kill typhoid germs in thirty minutes. The Rideal-Walker carbolic acid coefficient is 94.

Acids, Metallic Salts, Alkalis, and Metals

Germicidal Power of Acids and Metallic Salts.—The general rule appears to be that in each of these cases the germicidal power depends to a very large extent on the degree of **ionisation** and on the specific properties of the individual ions.

Thus it has been proved in the case of acids that, other things being equal, the germicidal value of an acid depends not so much upon the amount of alkali required to neutralise it as upon its degree of ionic dissociation.

The same applies to metallic salts. In general the metallic ion possesses a distinct germicidal value, and the more highly that they are dissociated at a given concentration the greater their germicidal value.

This general principle tends to be obscured by the fact that several salts and acids possess an inherent toxic effect on bacteria, quite independent of their degree of ionic dissociation. Moreover, some disinfecting salts are occluded or absorbed by solid substances accompanying bacteria, and so are prevented from exercising their full germicidal value.

The relationship between the chemical nature of the disinfectant employed and its disinfecting powers is, therefore, a very complex one, but much light has been thrown on the subject by researches carried out by Paul, Kronig, Sawey, and others between 1807 and 1900 (see *Pharm. Journ.*, 1900), to whose papers the reader should refer for further particulars.

Extended research has shown that metallic salts rank highest as germicides for spores (see Chick and Martin, *Journ. of Hygiene*, 1908, p. 634, and B.S. 808, 1938).

Boric Acid (H_3BO_3) has only a very small germicidal value (Rideal-Walker carbolic acid coefficient less than 0.1) and so cannot be considered to be a disinfectant.

Its chief value lies in its considerable power of preventing bacteria which attack food from developing. Thus, according to Rideal and Foulerton, 3 parts of boric acid and 1 part of crystallised borax added to 8,000 parts of milk prevented it from becoming sour for twenty-four hours, and no ill effects on the digestion appear to follow its use in moderate quantities. The use of boric acid is now prohibited in Britain, but it is still the main preservative employed in preserving cream (0.25–0.5 per cent. boric acid), butter, and margarine (0.5 per cent. boric acid) in other countries.

Usually mixtures of boric acid and crystallised borax are employed.

Sodium borofluoride ($NaBF_4$), under the name "**pyriat**," has been used as a food preservative.

Osmic acid is a very powerful germicide, being very poisonous and a powerful oxidiser, but is too expensive to be widely used.

Carbonic acid, carbon dioxide, has a distinct antiseptic action, since CO_2 under pressure preserves food, and many aerated waters seem to be almost completely sterilised

Fluorides and **hydrofluoric acid** (HF) are valuable antiseptics in that they inhibit the growth of various injurious organisms, although their direct germicidal value is small. Hydrofluoric acid and its salts (especially ammonium fluoride) have long been used in the brewing industry in order to check side fermentations and disinfect rubber hose, etc., 0.5-1 per cent. NH_4F being efficient for the purpose. For further details see **Martin's** "Industrial Chemistry: Organic," under **Fermentation Industries**.

Hydrofluoric acid and fluorides cannot be used for food preservation as they cause digestive disturbances.

Hydrofluorsilicic acid (H_2SiF_6) has been used as an antiseptic under the names of "**keramyl**" (25 per cent. H_2SiF_6) and "**montanin**." The sodium salt (Na_2SiF_6) has been used for the same purpose under the name "**salufer**."

Hydrocyanic acid (HCN) and its **sodium** and **potassium salts** are extensively used as insecticides and fungicides (see this volume under **Insecticides and Fungicides**), but are not nearly so effective towards bacteria and similar lower organisms.

Nitric acid and **oxides of nitrogen** are violent disinfectants, but their corrosive action, and also the extremely poisonous nature of these substances (breathing oxides of nitrogen may cause inflammation of the lungs, and even death), has caused their use for this purpose to be extremely limited. The cost of disinfection is very high.

Chromic acid is a very powerful germicide, instantly oxidising and coagulating albumen. The substance, however, is too expensive, too corrosive, and too poisonous for general use as a disinfectant and preservative.

Sulphuric acid is distinctly antiseptic and, when present in sufficient quantities, is also a disinfectant.

Thus, 0.05 per cent. disinfects iron pipes without markedly corroding the iron. 0.04-0.08 per cent. can destroy cholera germs in sewage. According to Rideal 0.035 per cent. sulphuric acid destroys typhoid germs in thirty minutes, 0.07 per cent. in fifteen to forty-five minutes. 0.09 per cent. sterilises the drainage from hospitals.

Nearly all acids possess considerable disinfectant power, and very few bacteria will develop in acid solutions.

According to Paul, Krönig, and Sawey (*Pharm. Journ.*, 1900) the germicidal action of acids is proportional to their degree of ionisation in solution, except in certain cases where the acids exercise a definite poisonous action.

For example, Winslow and Lochridge found in the case of sulphuric and hydrochloric acid that 99-100 per cent. destruction of *B. typhosus* or *B. coli* was effected with either acid at the same concentration of dissociated hydrogen (the germicidal action not being proportional to the strength of the acids as reckoned in normality).

The alteration in the ionisation in a dilute acid solution, brought about by the addition of neutral salts of the acid, usually accounts for the alteration of the germicidal value.

There are, however, many disturbing factors to be considered. Thus, certain acids, quite independently of their degree of ionisation, exercise a specific toxic action (*e.g.*, HCN, HNO_3, $CCl_3.COOH$, HF, all act poisonously towards certain bacteria). Again, the absorptive effect of solids in suspension affect the results considerably. What has been thoroughly proved is that the acidity, as measured by titration with alkali, does not give the germicidal value of an acid solution.

Acid sodium sulphate, sodium bisulphate ($NaHSO_4$), has a considerable germicidal value (Rideal-Walker coefficient = 4.1). It has been widely used for sterilising water for army purposes, being applied in the form of effervescing tabloids both in the South African and the Russo-Japanese wars.

Rideal and Parkes (who introduced the substance for this purpose) showed that 15 grains of $NaHSO_4$ to a pint of water in fifteen minutes destroyed nearly all disease germs, as well as internal parasitic worms.

Sulphur dioxide has long been used as a disinfectant, being produced either by burning sulphur in air, or else by employing the liquefied gas in canisters. The latter method is preferable, as a regular supply of gas is assured, and there is no danger of fire.

Attention to certain details is necessary in order to secure good results. Thus the **dry gas** has little effect on bacteria and spores, but kills vermin of all kinds, and so is especially effective in combating insect-borne infection.

The wet gas is very much more germicidal in its action, but as a rule there is sufficient natural moisture in the air to make it act efficiently with only slight moistening. Thus, 1 lb. of sulphur burnt in a closed space of 1,000 cub. ft. dilutes the air with 1.15 per cent. of sulphur dioxide. 0.56 lb. of water is theoretically required to turn this into sulphurous acid, but owing to the water already in the air the additional moisture should only be applied by lightly spraying the surface or washing. Rideal found that when shallow pans of water were placed on the floor of a room with the object of supplying moisture, the sulphur dioxide contents were actually lowered (by water absorbing the gas) by over 50 per cent. in twenty-four hours, and disinfection was not complete.

Quantities Necessary for Disinfection of Rooms.—3¼ lbs. sulphur burnt per 1,000 cub. ft. in twenty-four hours killed germs like *B. typhosus* and *diphtheriæ*, but not *B. tuberculosis* in dried sputum, nor anthrax spores. According to Rosenau, 5 lbs. sulphur per 1,000 cub. ft. kills all spore-bearing organisms after sixteen hours' exposure. Of course the rooms must be sealed.

Employing liquefied SO_2 in canisters, one can reckon that 1 lb. of the liquid will yield 5½ cub. ft. of gas.

For **disinfecting the holds of ships**, sulphur is burnt in a special apparatus, and the issuing gases (containing air, SO_2, and a cloud of H_2SO_4 mist) are forced in until the SO_2 contents of the air shall reach 10 per cent. For details in use, see "The Local Government Board Reports."

Other Uses of Sulphurous Acid and Sulphites.—A solution of sulphur dioxide in water (sulphurous acid) is much used as a germicidal wash or spray in parasitic diseases like diphtheria, and is also applied internally in gastric fermentations, cholera, etc.

The solution and also bisulphites are widely used in the fermentation and food industries as a means of checking injurious fermentation.

Several preparations of sulphites have been placed on the market, *e.g.*, "Hawke's anti-ferment," "meat preserve crystals," etc.

There are, however, objections to the extended use of sulphites in this direction. According to Lehmann 0.004 per cent. will not injure health.

Durham (*Journ. of Hygiene*, April 1909) suggests the maximum legal limit allowed should be 0.01 per cent. of "total sulphur dioxide."

Disadvantages of the Use of Sulphur Dioxide.—One of the main **disadvantages** of the use of sulphur dioxide for disinfecting purposes is that it is corrosive; it attacks metals and organic substances (being of an acid nature), and a great deal is absorbed by the calcareous plaster, of which the ceiling and walls are usually composed. Moreover the substance has little penetrating power, and cloth, bedding, and similar materials cannot be easily sterilised by it, the usual practice being to remove them and sterilise by heating in boilers. The fibres of textiles, too, are often rotted after treatment with sulphur dioxide, owing to the free sulphuric acid produced gradually disintegrating the material.

Moreover the gas is poisonous. It has been found that about 5 per cent. in the air has caused death. 0.5 per cent. can be breathed for some time, and a higher percentage than this can be tolerated by breathing through a wet cloth soaked in washing soda.

Sulphur is principally used as an insecticide and fungicide, its use in this respect being fully discussed in the section on **Insecticides and Fungicides**, which see. The same applies to the **polysulphides**.

Arsenic is also principally used as an insecticide, it being widely employed for sheep-dips and similar preparations, the preparation and uses of which are described in the section on **Insecticides, Fungicides, and Sheep-Dips**. Arsenic acts more injuriously on the higher forms of life than on the lower. The medicinal organic compounds, introduced by Ehrlich and others for various parasitical diseases, are treated of in **Martin's** "Industrial Chemistry: Organic."

Lime, quicklime (CaO), has a strong germicidal action when in a dry condition, a fact which has been taken advantage of for centuries in the practice of burying the bodies of victims of plague and cholera in quicklime, and in the periodical whitewashing of buildings.

Unfortunately the disinfecting power of lime is not so great as was formerly supposed.

Thus it requires 74 parts of CaO (in the form of milk of lime) per million of water to destroy typhoid bacteria, while no less than 247 parts per million are required for destroying cholera bacteria, some hours' contact being required in each case. The "excess lime" method of sterilising drinking water is referred to at length in Vol. I. of this work under **Water**.

Two per cent. of dry quicklime and some hours' contact are required to sterilise cholera discharges.

It has been proved that disinterred infected bodies, which have been buried in lime, will retain the disease spores alive for a long time; these may again become active and cause infection.

Sodium and potassium hydroxides act as sterilisers when present in the proportion of 3-5 per cent. Warm solutions (60° C.) cause the death of most organisms in three or four minutes.

Sodium and potassium carbonates are also antiseptics when present in solution to the extent of 6-15 per cent. The hot solutions (50°-60° C.) cause the death of most germs in a few minutes.

Soaps are also slightly antiseptic (see **Martin's** "Industrial Chemistry: Organic," under Soap).

Salt, or strong brine, acts as an antiseptic—that is, prevents injurious bacteria from developing, and hence the ancient practice of salting beef, etc. Wounds may be treated with brine to prevent the development therein of dangerous organisms. Salt, however, is not a disinfectant—that is, it does not actually destroy disease germs. Thus it has been shown that a 50 per cent. salt solution does not kill the spores of ordinary moulds.

The common practice of washing out milk utensils, cans, etc., with brine has, therefore, little value from the disinfecting point of view.

Copper and Copper Salts

Copper salts are all powerful germicides, the efficiency of the soluble copper salts depending upon their percentage of copper. *Copper sulphate*, being the cheapest, is the most usual one employed of the copper salts. It has a Rideal-Walker coefficient of 2.0 (calculated as $CuSO_4$). The main use of copper sulphate occurs in agriculture for killing parasites infesting vegetation. The best known preparation is called **Bordeaux mixture**, and as the matter is fully discussed in the section on **Insecticides, Fungicides, and Sheep-Dips**, we refer the reader thereto for further information.

It has been proved that the disinfection of excreta, etc., with such large quantities as 5-10 per cent. copper sulphate is not satisfactory. According to American authorities [see Bull. U.S. Dept. of Agric., No. 100, **1906**; see also U.S. Geological Survey, Water Supply Paper, 229, p. 32 (1909)], disinfection by means of copper sulphate is not so efficient as that caused by chlorine compounds, and is very much more expensive. However, a soluble disinfectant for stables and drains, consisting of about 75 per cent. of copper sulphate and sulpho-carbolate, and containing some free sulphur dioxide, has been sold under the name of "**microsol.**"

Cuprous chloride (Cu_2Cl_2) is considerably more germicidal in its action than copper sulphate. Thus Kroncke completely sterilised Elbe water (containing 50,000 organisms per c.c.) by treating with 50 parts per million of cuprous chloride, adding 20 parts of ferrous sulphate, standing for six hours, and then precipitating all metal by mixing with 10 parts lime. On filtering through sand the water was perfectly colourless and sterile.

Metallic copper appears to possess sterilisation properties. Thus the U.S. Department of Agriculture (1904) states that 1 sq. cm. of bright copper per 100 c.c. of water destroys *uroglena*, some forms of *spirogyra.*

Kraemer, Rideal and Baines (*Journ. San. Inst.*, 1904, p. 594), and B. Smith (*Journ. Prev. Med.*, July 1904) have extended these observations, and confirmed them. Thus it was proved that by immersing strips of copper of 2 sq. cm. to each 100 c.c. water (*i.e.*, 3½ sq. in. to each quart) typhoid and colon bacilli were destroyed in four to twenty-four hours (the length of time given by the different authorities varies greatly), and that with water containing over 1,000 ordinary organisms per c.c., only eight organisms per c.c. were left after twenty-four hours.

The germicidal effect of copper on many algæ and bacteria is believed to be due to the passing of the copper into colloidal solution.

Mercury and Mercury Salts

Mercury salts are nearly all possessed of a high germicidal power.

According to Krönig and Paul (1897) the germicidal power depends almost solely upon the **metallic ion**, and is proportional to its degree of ionisation.

Thus, on comparing equivalent solutions of mercuric chloride, bromide, and cyanide, he found that the first is more germicidal than the second, and the second than the third, and that this order corresponds with the degree of ionisation of these substances, the cyanide being almost non-ionised.

Again he showed that on comparing solution of mercuric chloride in water of different strengths, a solution of one part $HgCl_2$: 1,000 water is more than twice as active as one part $HgCl_2$: 500 water, this enhanced activity corresponding to the increased dissociation of the mercury salt in the diluter solution.

Mercuric chloride ($HgCl_2$), long known as "corrosive sublimate," is one of the most powerful of disinfectants known, and formerly a 0·1 per cent. solution was taken as the standard of comparison of other disinfectants. The Rideal Walker coefficient is 400-4,000.

The solution recommended for disinfecting purposes by the **Local Government Board** consists of mercuric chloride, ½ oz.; hydrochloric acid, 1 fluid oz.; aniline blue, 5 grains; water, 3 galls.

The aniline blue is added for colouring the liquor, so as to prevent it getting into potable waters, etc., by accident.

Mercuric chloride is largely used in museums and similar institutions for preserving stuffed animals and specimens. Mercuric chloride has never come into extended use as a general disinfectant for the following reasons:—

(1) The substance is very expensive; (2) it is extremely poisonous to higher animals and plants, and hence is dangerous to use; (3) it is an irritant to wounds; (4) it is often destroyed chemically, the mercury being precipitated in the form of insoluble salts, by alkalis, by many salts, hard water, sulphides, and organic bodies; so that the substance is liable to be removed from solution before it has done its germicidal work—time being an important factor in this.

In particular, the substance combines with albuminous matter, forming an insoluble coagulum. Consequently it may form a pellicle over organisms without killing them, and cannot be used for disinfecting excreta and sputum, owing to its penetration being stopped by the protective albuminoid coagulations. The soluble albumen contained in blood serum precipitates mercuric chloride, and so reduces its efficiency.

The addition of ammonium or sodium chloride somewhat increases the stability of $HgCl_2$ solutions, but considerably diminishes its germicidal activity, no doubt, by lessening the ionic dissociation of this substance.

Mercuric bromide ($HgBr_2$) is less germicidal than mercuric chloride, and so is seldom employed.

Mercuric iodide (HgI_2) is a powerful germicide, and finds some use under the name of "**iodic hydrarg,**" which consists of a solution of mercuric iodide in potassium iodide.

Mercuric iodide is less irritant to wounds than mercuric chloride, and does not coagulate albumen in the same manner. Hence it has been incorporated into several antiseptic ointments and soaps.

Mercuric cyanide ($Hg(CN)_2$) is no less than four times less germicidal than mercuric chloride, and so is seldom employed. **Mercury oxycyanide**, however, finds considerable application in surgery since, unlike mercuric chloride, it only slightly precipitates albumen. A solution of 1 : 1,500 forms a faintly alkaline antiseptic non-irritant solution, suitable for disinfecting surgical instruments.

Mercuric zinc cyanide has been widely used for disinfecting surgical instruments under the name of "Lister's Antiseptic."

Mercuric ethylene diamine sulphate has been used as a hand disinfectant under the name "**sublamen**." It does not coagulate albuminoid matter, is less irritant than mercuric chloride. It is readily soluble in water.

Sodium hydroxy mercury benzoate has been suggested as a powerful disinfectant.

Mercury salicylate is also a disinfectant.

"**Protectyl**" consists of a solution containing 0.2 per cent. Hg, 1 per cent. salicylic acid, 3 per cent. gelatine, and 95.8 per cent. water.

Metallic mercury has a powerful germicidal value, and was much used in a finely divided form for certain parasitic diseases, such as syphilis. Many well-known ointments contain metallic mercury.

Silver Salts

Silver Nitrate is a very powerful germicide, possessing a Rideal-Walker coefficient of 16. A 0.1 per cent. solution will kill *B. coli* and *S. py. aureus* in twenty-four hours. 0.5-2 per cent. solution kills the same germs in two to five minutes.

Although silver nitrate enjoys considerable vogue in surgical practice for painting and spraying skin surfaces infected with various parasitical diseases, yet it has never come into extended use as a disinfectant because:—

(1) It is very expensive; (2) it combines with albumen, and is precipitated by many salts, including chlorides. Rideal proved that a very small amount of chloride added to a 0.1 per cent. solution entirely upset its disinfecting powers.

Silver fluoride is a powerful non-toxic and easily soluble germicide much used in 0.1-0.02 per cent. solutions as an antiseptic in diseases of the urinary organs. It has been sold under the name "Tachiol."

Organic Silver Salts.—A great number of these have been placed on the market as disinfectants. The great advantage of employing organic silver salts is that they do not, as a rule, coagulate albumen, as their silver is not completely precipitated by chlorides, and they are less irritant than silver nitrate.

Silver citrate is used as an antiseptic dust for wounds under the name "Itrol."

Silver lactate is used as an antiseptic injection under the name "Actol."

Ethylenediamine-silver-phosphate has been used for a similar purpose under the name "Argentamine."

Compounds of silver with **albumen, casein, wheat gluten,** etc., have been put on the market under the names "**largin**," "**argonine**," "**agyrol**," "**protargol**," and some of these have a considerable germicidal value.

They have been used especially for destroying ophthalmic disease organisms, and in diseases of the urinary organs. Silver salts in solution in water, with the addition of ephedrine, are used in the treatment of nasal catarrh.

Zinc Salts and Zinc

Zinc chloride ($ZnCl_2$) has a feebly disinfecting power (Rideal-Walker coefficient 0.15), and was at one time widely used under the name of "Burnett's Fluid." It is now little used. **Zinc chloride** has also been used for injecting into timber for the purpose of preserving it.

Zinc sulphate ($ZnSO_4$) has also some germicidal action (Rideal-Walker coefficient 0.09), but is now little used.

Metallic zinc is said to possess a very considerable germicidal action. Thus agitation of water with granulated zinc is stated to destroy *B. coli* and *B typhosus* in a few hours. Margosches sterilised water by agitating it with zinc dust, lime, and charcoal.

The presence of air or oxygen seems necessary.

Aluminium Salts and Aluminium

Aluminium chloride ($AlCl_3$) has a feeble disinfecting action, less than that exerted by copper sulphate and greater than that of zinc chloride.

Metallic aluminium seems to have a considerable sterilising effect on water. On running water down aluminium gutters the number of bacteria considerably decreases. The subject is discussed in Vol. I. of this work under **Water.**

Iron salts, especially ferrous sulphate, have been applied for disinfecting purposes, but according to Rideal they are ineffective. **Metallic iron**, however, appears to possess some germicidal value.

PART III.—ANTIBACTERIAL DRUGS AND ANTIBIOTICS

Perhaps the greatest advance ever made in the field of germicidal agencies has been that during the past twenty years with the discovery of substances that could be introduced into the body by mouth or by injection, and capable of destroying diseases caused by bacteria or viruses without harming human or animal life. These substances fall naturally into two classes according to their origin. In the first class are a group of synthetic organic compounds related to **sulphanilamide** and in the second class are natural substances derived from moulds, of which **penicillin** was the first to be produced and used on a large scale. These two classes of compounds have been successfully used against many of the worst diseases known to man, including streptococcus infections, pneumococcic pneumonia, meningitis, and erysipelas, gonorrhœa, syphilis, anthrax, septicæmia, gas gangrene, staphylococcus, and tuberculous meningitis.

Sulphonamides. Sulphanilamide itself is a derivative of aniline with the formula $C_6H_4(NH_2)(SO_2NH_2)$, and its value in combating diseases caused by bacteria was first noted by Trefouel, Nitti, and Bovet, of the Pasteur Institute. Since then the use of sulphanilamide and its derivatives have developed rapidly and they have been particularly effective in the treatment of pneumonia, influenza, and infantile paralysis. These substances may be taken through the mouth and rapidly find their way to all the body tissues, being finally eliminated in the urine in about twelve hours. Large volumes of water are usually taken by the patient during this treatment to assist the action of the kidneys. Sulphapyridine is very useful in children's pneumonia and in staphylococcus infections, but kidney complications sometimes follow its use. Other derivatives found to be of special value are sulphadiazine for pneumonia in animals, sulphaguanidine and succinylsulphathiazole for intestinal infections of animals and poultry, and sulphanilamide and sodium sulphathiazole for the treatment of wounds.

Antimalarials.—These are a group of substituted diguanides, of which paludrine is perhaps the most important, since it is relatively free from side effects and more active than either quinine or mepacrine. Paludrine has the formula $C_6H_4Cl.NH.C(:NH).NH.C(:NH).NHPr^{\beta}$, and has a true prophylactic effect in malignant malaria and a partial effect in **Plasmodium vivax** infections.(14)

Antibiotics.—Penicillin was the first of the antibiotic substances found, and it is still the most used. It was discovered by Sir Alexander Fleming, in 1929, when he observed that the mould **Penicillium notatum** inhibited the growth of the pathogenic organism **Staphylococcus aureus.** The commercial development of penicillin was rapid during the years 1939–41, largely through the efforts of Florey and Heatley of Oxford, and Moyer at the U.S. North Regional Research Laboratory, Illinois. Moyer found that the addition of corn steeping liquor to the medium on which the mould grew increased the rate of production ten times, and this became the standard method of preparation. More recently Stone and Farrell (15) have developed a synthetic medium, which is slower than corn steep liquor, but which makes purification simpler. The addition of phenylacetamide with leucine or cystine improves the yield. Penicillin is recovered as the sodium or calcium salt of the acids in the broth. These consist of a pale brown powder containing from 10 to 30 per cent. of sodium penicillin (120 to 500 Oxford units per mg.) which is stable at temperatures below 10° C. The material is tested for conformity to the U.S. Food and Drug regulations for use in the U.S.A. In England penicillin was brought within the scope of the Therapeutic Substances Act, 1925, by Regulations made in 1944 and subsequently amended so as to ensure that penicillin and its preparations satisfy the requirements of the Therapeutic Substances (Amendment) Regulations, 1946 (S.R. & O. 1946, No. 467), as amended by the Regulations of 1948 (S.I. 1948, No. 2418). This Act restricts the sale of supply of penicillin to medical or dental practitioners and prohibits the administration of penicillin except by a practitioner. The Editorial Board of the American Monograph on the Chemistry of Penicillin,(16) published in 1947, described in detail a work carried out in the U.K. and U.S.A. during the war on the structure of penicillin and the attempts to synthesise the material. Useful summaries of the main conclusions resulting from this work have been published by Chain (17) and Cook.(18)

Streptomycin.—Streptomycin is the most effective agent yet discovered for the treatment of tuberculosis. The Medical Research Council (19) has described the results of the treatment of tuberculous meningitis, a disease previously invariably fatal, in which 30 cases recovered out of 105 cases treated. The Council has also published a report (20) on the treatment of pulmonary tuberculosis with the drug. Streptomycin may be prepared by the surface culture of **Actinomyces griseus** on a yeast medium.(21) The Merck research group (22) have proposed a full structure for streptomycin based on evidence supporting attachment of streptobiosamine to carbon atom 4 of streptidine. Evidence is available to show that streptidine is probably 1:3-diguanido-2:4:5:6-tetrahydroxycyclohexane.(23)

Other Antibiotics.—Other antibiotics that have been developed and used in recent years include: **Aerosporin,** produced from **Bacillus aerosporus** and said to be effective against several Gram-negative and Gram-positive organisms; **Chloromycetin,** active against **Mycobacterium tuberculosis** and Gram-negative bacteria; **Auromycin**, produced by **Streptomyces aureofaciens** and said to be active, *in vitro*, against penicillin- and streptomycin-resistant organisms and, *in vivo*, against the viruses **lymphogranuloma venereum** (24) and psittacosis. In humans it has been used effectively for the treatment of spotted fever, ocular infections, primary atypical pneumonia, and urinary tract infections. The importance of moulds as sources of antibiotics has declined recently, since the most promising substances discovered of late have been obtained from actinomycetes or bacteria.

Quantitative aspects of Antibiotics.—According to Robinson,(25) the amounts of antibiotics produced in the U.K. and U.S.A. have increased enormously in recent years. Thus, the amounts of penicillin produced in the two countries in 1944 were 36,000 and 1,600,000 mega-units respectively, whilst for the first ten months of 1948 the corresponding figures were 7,300,000 and 76,600,000 mega-units. In the U.S.A. the production of streptomycin, which began in 1945, amounted in the first ten months of 1948 to 27,000 kg. In 1946 the sales values of the two antibiotics were $89,000,000, and $6,000,000 respectively. In contrast, the value of all the sulphonamides sold in the same period was $23,300,000.

REFERENCES

(1) Rideal and Walker, *J. Roy. San. Inst.*, 424 (1903).
(2) B.S. 541, "Technique for determining Rideal-Walker Coefficient" (1934).
(3) Chick and Martin, *J. Hygiene*, 634 (1908).
(4) B.S. 808, "Modified Technique for Chick-Martin Test" (1938).
(5) B.S. 1013, "Disinfectants and Sanitary Powders" (1946).
(6) A. T. Palin, *J. Inst. San. Eng.*, July 1945.
(7) R. M. Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929); **53**, 912 (1931).
(8) P. C. Laux, *J.A.W.W.A.*, **32**, 1027 (1940); and J. B. Nickel, *W. Wks. and Sew.*, **89**, 531 (1942).
(9) C. Lea and A. J. Mills, Ann. Conf. N.A. Bath Supers., 1949.
(10) A. T. Palin, *J. Inst. Water Eng.*, **III**, **2**, 100 (1949).
(11) J. S. Zinsser, *Chem. and Eng. News*, **21**, 1159 (1943).
(12) R. D. Coghill, *Chem. and Eng. News*, **22**, 588 (1944).
(13) Adams *et al.*, *Ann. Trop. Med. Parasitol.*, **39**, 208 (1945).
(14) A. Spinks *et al.*, *Biochem. J.*, **40**, 1 (1946).
(15) R. W. Stone and M. A. Farrell, *Science*, **103**, 504 (1946).
(16) *Science*, **106**, 653 (1947).
(17) E. Chain, *Endeavour*, **7**, 83, 152 (1948).
(18) A. H. Cook, *Quart. Rev.*, **2**, 203 (1948).
(19) *Lancet*, **1**, 582 (1948).
(20) *Brit. Med. J.*, **2**, 769 (1948).
(21) G. A. le Page and E. Campbell, *J. Biol. Chem.*, **162**, 163, 403 (1946).
(22) F. A. Kuehl *et al.*, *J. Am. Chem. Soc.*, **69**, 1234 (1947).
(23) H. E. Carter *et al.*, *Science*, **103**, 540 (1946).
(24) L. T. Wright *et al.*, *J. Am. Med. Assn.*, **138**, 408 (1948).
(25) F. A. Robinson, *Applied Chem. Reports*, XXXIII, 603 (1948).

SECTION LIII

FUNGICIDES, SHEEP-DIPS, AND INSECTICIDES

By Geoffrey Martin

Revised by Wilfrid Francis

LITERATURE

E. Bourcart.—"Insecticides, Fungicides and Weed Killers." London.

T. F. West and G. A. Campbell.—"D.D.T., the Synthetic Insecticide." London, 1946.

W. C. Harvey and H. Hill.—"Insect Pests." London, 1940.

D. E. H. Frear.—"Chemistry of Insecticides and Fungicides." 1942.

F.I.A.T. 949.—"Organic Chemical Intermediates for Insecticides, Fungicides and Rodenticides." 1946.

B.I.O.S. 1095.—"Developments in Methods for the Control of Plant Pests in Germany." 1947.

B.I.O.S. 1480.—"Manufacture, Formulation and Application of Major Pest Control Products." 1947.

B.I.O.S. 714.—"The Development of New Insecticides." 1947.

FUNGICIDES

Fungicides.—Fungicides and insecticides are used for the control of fungal or insect pests in farming, horticulture, husbandry, and veterinary practice. Fungicides are usually inorganic compounds or mixtures, though the more powerful disinfectants and certain of the insecticides may often be used as fungicides. More usually they are salts of copper, zinc, mercury, fluorine, and sulphur, or mixtures of sulphur or sulphides. Solutions of tar acids and their sodium salts are also used. The more important fungicides used to-day are listed below, with some details of their method of preparation and use.

Copper Compounds

Bordeaux Mixtures.—One of the most valuable fungicides for plant diseases is Bordeaux mixture, consisting of copper sulphate and slaked lime.

Formula I.—Copper sulphate, 6 lbs.; lime, 4 lbs.; water, 50 galls.
Formula II.—Copper sulphate, 5 lbs.; lime, 5 lbs.; water, 50 galls.
Peach Bordeaux Mixture.—Copper sulphate, 3 lbs.; lime, 9 lbs.; water, 50 galls.
Soda Bordeaux Mixture.—Copper sulphate, 6 lbs.; caustic soda, 2 lbs.; water, 50 galls.
Potash Bordeaux Mixture.—Copper sulphate, 6 lbs.; caustic potash, 2 lbs.; water, 50 galls.
Soap Bordeaux (increases spreading power).—Ordinary hard soap is dissolved in water and added at the rate of 4 lbs. to the barrel of solution.

Manufacture.—In order to make small quantities, two half barrels are made by sawing a barrel through the middle. In one half barrel is placed the copper sulphate and 25 galls. of water. In the other is the lime and also 25 galls. of water. The contents are stirred until as much has dissolved as possible.

The two half-barrel tubs are placed on a platform, and by means of hose or spigots the two solutions are allowed to flow together into a barrel placed below.

The Bordeaux mixture is then strained through a brass wire strainer of eighteen to twenty meshes to the inch.

Copper Sulphate solution may be used as a spray for mildew and insect pests on fruit trees and for ridding wheat and barley of "smut." Mixed with sulphonated tars or resins and sulphur or arsenical preparations, copper sulphate effectively destroys mildew on vines.

Cheshunt Compound. Mix two parts of copper sulphate with eleven parts of fresh ammonium carbonate and store in a closed vessel for twenty four hours. Use one ounce of the mixture to two gallons of water for watering seeds and young plants to prevent damping off.

Mercuric Chloride (corrosive sublimate) is used in very dilute solution (1 part in 1,000) to disinfect knives used in cutting out pear blight and similar diseases.

Sodium fluoride is also a powerful fungicide.

Sulphur Mixtures

Sulphur, especially in the form of a powder, "flowers" of sulphur, is used as a fungicide, especially as a remedy for mildew. "Flour" of sulphur is not so finely divided as "flowers," and so is not so good. The heating pipes of greenhouses are often painted with a paste of flour of sulphur and water.

Sulphur and Resin Solution. Sulphur (flowers or flour), 16 lbs.; resin (finely powdered), ½ lb.; caustic soda (finely powdered), 10 lbs.; water, 6 galls.

Mix the sulphur and resin, place in a barrel, and make into a thick paste by adding 3 quarts of water. Now stir in the caustic soda. The mass, after a few minutes, begins to boil vigorously, turning a reddish brown. It should be thoroughly stirred, and after boiling has ceased 2 galls. of water are added, the liquid is poured off into another vessel, and sufficient water to make 6 galls. is added.

This solution is used (1 : 50 galls. of water) for spraying plants and soaking seeds.

Potassium Sulphide Fungicide. Dissolve 1 oz. of potassium sulphide (liver of sulphur) in 3 galls. of water and use immediately. Mixture deteriorates rapidly on standing.

Liver of sulphur is made by heating together sulphur and potassium carbonate in a closed vessel.

Lime Sulphur.—This is a valuable fungicide for both winter and summer use. The mixture may contain 8 lbs. of sulphur (flowers, flour, or ground), 8 lbs. of fresh stone lime, and 50 galls. of water.

Preparation.—The lime is placed in a barrel and enough water (6 galls.) is poured on to almost cover it. As soon as the lime begins to slake, run in the sieved sulphur powder, stir continually, and add 3–4 galls. more water so as to form a thick and then a thin paste. The heat evolved by the slaking lime should heat the water almost to boiling for several minutes.

Finally, water is added to cool the hot liquid, and it is run through a strainer into a tank, diluted, and applied.

Lime sulphur is valuable in cases of chrysanthemum rust, rose mildew, club root, and similar plant diseases. Liver of sulphur may be used as alternatives to the lime sulphur for the rusts, whilst mercuric chloride should be used as an alternative for club root. Cleansing the ground with lime or fumigation with formaldehyde is an additional precaution, particularly the latter, in greenhouse applications.

Organic Fungicides

Formaldehyde (see **Martin's** "Industrial Chemistry: Organic"), either in solution (1 lb. formalin to 50 galls. of water) or gasified, is often used for treating seeds, wheat, or oats. Formalin, if used in too strong a solution, or if the grain is soaked too long, may destroy the germinating power of grain.

Tar Acid Mixtures.—All solutions of carbolic oil, phenols, cresols or their salts, either alone or mixed with sulphur, or lime sulphur washes, are used to destroy fungoid growths on trees. They may be used in much stronger solutions than when similar solutions are used as insecticides, for example as sheep dips, and are best applied as winter sprays.

Nicotine solutions, used alone or mixed with sulphur, are effective against mildew and moulds, and may be used in dilute form for summer sprays, both as a fungicide and as an insecticide.

A wide range of organic insecticides, weed-killers, and fungicides has been developed during the last ten years, of which the following products, manufactured by the Monsanto Chemical Company, are typical:—

MODERN FUNGICIDES, INSECTICIDES, AND WEED-KILLERS

Trade Name.	Chemical Name.	Type.	Uses.
Nifos-T	Tetraethyl-pyrophosphate	Organic phosphorus insecticide	When formulated, controls mites, thrips, scale, aphides, moths, and flies. Compatible with some organic insecticides
Niran (Parathion)	Diethyl paranitro-phenyl-thiophosphate	Organic phosphorus insecticide	When formulated, controls aphides, mites, grasshoppers, scale, and thrips. Compatible with other insecticides and fungicides
2.4-D	2.4-Dichlorophenoxy-acetic acid Sodium 2.4-Dichlorophenoxy-acetate-monohydrate	Hormone-type herbicide	Toxic to non-grassy plants. Used for weed control in grassland, turf, and cereals
Santobrite	Sodium pentachloro-phenate	Contact herbicide, water soluble	For control of broad-leaved weeds. Preservative for wood, textiles, etc.
Santophen-20	Pentachlorophenol	Formulated as an oil emulsion spray	Toxic to broad-leaved weeds and grasses. Preservative for wood
Thiurad	Tetramethyl-thiuram-disulphide	Fungicide and seed dressing agent	
Methasan	Zinc dimethyl-dithio-carbamate	Fungicide used for the control of early blight in vegetables	
Diphenyl	Diphenyl	For impregnation of fruit wrapping paper	
Permasan	Pentachlorophenol	Oil solution of pentachlorophenol. Protection against bacteria or fungi by immersion or spray	

SHEEP-DIPS

The sheep-dips most commonly used contain sulphur, arsenic, carbolic acid, and sulphur, and are used to destroy scab and ticks.

The dips containing sulphur are the best, the sulphur being retained in the wool (being non-volatile and non-soluble) for a longer period of time than the scab parasites remain alive away from their hosts.

Lime and Sulphur Dip.—The following is a typical lime and sulphur dip which has been used in various parts of the world:—

Flowers of sulphur	20 lbs.
Fresh slaked lime	10 lbs.
Water	100 galls.

Preparation of Lime and Sulphur Dips.—8–11 lbs. of unslaked lime are placed in a pail and enough water is added to slake the lime and form a thick paste. One pint of water will slake 3 lbs. of lime. Sift into the lime paste three times as much flowers of sulphur as was used of lime, and stir the mixture. Next place the sulphur-lime paste in a kettle or boiler with 25–30 galls. of boiling water, boil the mixture for two to three hours, stirring continuously, and replacing evaporated water.

The sulphur should disappear from the surface and a solution of a chocolate-brown colour should result.

Now pour into a settling tank or barrel and allow to settle four hours.

The barrel or tank should have a spigot inserted 3–4 in. from the bottom, so as to run the liquid out without disturbing the sediment.

When fully settled run the clear liquid off through a filter made of ordinary sacking into the dipping vat for sheep, and add enough warm water to make 100 galls. The sediment left in the barrel and filter sack **must not be used for dipping cattle.** It may, however, be mixed with water and used as a disinfectant.

Use of Lime and Sulphur Dips.—When properly made and used, these dips are most efficient scab destroyers.

The wool is always injured to a slight extent by the use of such dips, but when used upon shorn sheep the injury is negligible. On long wool, however, the injury is greater, being most pronounced on fine wool and less so on coarse wool. The injury consists in a change in the microscopic structure of the fibre, caused by the caustic action of the liquor. Improperly made and used lime and sulphur dips are, however, both injurious and dangerous.

Tobacco and Sulphur Dips.—The proper preparation of a lime and sulphur dip requires at least two hours' boiling of the mixture. In certain districts of America and Australia, however, where fuel is scarce and facilities for boiling are not at hand, the use of a **tobacco** (or **nicotine**) **and sulphur dip** is growing, since these can be made without lengthy boiling.

The advantage of these dips is that two of the best scab remedies, namely, tobacco (nicotine) and sulphur, are used together, both of which kill the parasites, while the sulphur remains in the wool, and protects for some time against reinfection.

Nicotine (see **Martin's** "Industrial Chemistry: Organic"), an alkaloid contained in tobacco, is the poisonous active principle of the tobacco. This poison when applied externally to animals may cause nausea, fainting, and even death.

A solution containing from 30–60 parts of nicotine in 100,000 parts of water makes a slow but sure acting sheep-dip. The percentage of nicotine, however, varies greatly in different varieties of tobacco and in the different parts of the tobacco plant. There is more nicotine in the leaves than in the stem. Hence it is usual to use an extract of tobacco, or a nicotine solution, on account of the ease with which these extracts dissolve in water.

Manufacture.—An efficient tobacco dip should contain at least 0.0007 per cent. of nicotine. Sufficient nicotine would therefore be obtained for 100 galls. (800 lbs.) of dip by using 1 lb. of a 40 per cent. solution of nicotine. Hence the formula for an efficient dip would be—

Nicotine	0.56 lb.
Water	100 galls.

The nicotine solution or tobacco extract should not be added to the dip until just before it is ready for use. The dip should be thoroughly stirred.

The dip should never be heated above 110° F. (44° C.) after the nicotine has been added, as the nicotine can volatilise and weaken the dip.

Arsenical Dips

Formulæ: (1) 3 lbs. each of arsenic oxide, soda ash, soft soap, and sulphur (a pint or two of naphtha is sometimes added) is dissolved in 10–20 galls. of boiling water, and cold water is added to make 120 galls. Keep head of sheep out of bath.

(2)	Commercial pure sodium arsenite	14 lbs.
	Ground roll sulphur	34.5 lbs.
	Water	432 galls.

The arsenite of soda is mixed with the sulphur before adding the water.

The **disadvantages** of arsenic dips are: (1) Danger as a deadly poison; (2) drying effect on wool; (3) weakens the fibre of wool in one particular spot near the skin; (4) does not tend to increase the growth of the wool; (5) sometimes injures the sheep. The advantages are its excellent scab-curing qualities.

Carbolic Dips

These dips act very quickly in killing mites (quicker than tobacco or sulphur dips), but unfortunately the wash soon leaves the sheep, which is, consequently, not protected from reinfection in the pastures. Hence it is advisable to add 1 lb. of flowers of sulphur to every 6 galls. of dip as a protection against reinfection.

INSECTICIDES

Most of the mixtures described under fungicides and sheep-dips have also been used as insecticides, though the solutions are usually diluted when used as insecticides and the powders mixed with inert diluents. Many of the substances already described suffer the disadvantage of being highly poisonous and can therefore not be used safely as insecticides for humans or for foodstuffs grown for human or domestic animal consumption. Nevertheless, some of the more poisonous compounds are still used in some agricultural applications, as will be seen from the following summary of insecticides in common use to-day.

Arsenic Compounds.—These include: solutions of **arsenious oxide** in caustic soda, for use against insect pests such as the boll weevil; **calcium arsenite and arsenate,** for leaf worm and boll weevil on cotton plants; **lead arsenate** for insect pests and fungal growths; **copper acetoarsenite,** or **Paris green,** as an insecticide for spraying fruit trees infested with caterpillars and against the larvæ of leather jackets. Paris green is also used mixed with bran as a powder for use against leather jackets and wood lice.

Naphthalene and Carbon Disulphide.—These are used for the sterilisation of soils and as insecticides against wire worms, leather jackets, cabbage fly, onion fly, and termites.

Sodium fluosilicate, mixed with slaked lime, is sometimes used in place of arsenical preparations for the same purposes.

Hydrogen cyanide and **formaldehyde** are both used as fumigants in greenhouses and are effective against red spiders and flies.

Derris Powder.—This is the dried root of the plant **Derris elliptica,** found in Malaya and the East Indies. The active principle is the resin rotenone, which may be obtained by extracting the dried root with trichlorethylene. The extracted root is almost as effective as the resin. The cultivation of Derris elliptica and other similar species is discussed fully in *Bull. Imp. Inst.*, **2,** 199, 1935. Derris may be applied as a powder or as a spray. To make the liquid spray, dissolve $\frac{1}{4}$ lb. of the powder in 12 galls. of water, and add $\frac{1}{2}$ lb. of soft soap. Derris is frequently mixed with other insecticides, such as pyrethrum powder, D.D.T., or Gammexane.

Pyrethrum powder is even more effective as an insecticide than derris powder and has the advantage over the newer insecticides, D.D.T. and Gammexane, in being almost instantaneous in its effect. The active principle is called pyrethrin, which is a mixture of complex organic acids and keto-alcohols. Because of its "knock-down" effect pyrethrum is frequently mixed with D.D.T., or Gammexane, in proprietory brands of insect powders. Because of their great value, demands for insect powders based upon pyrethrum, derris and lonchocarpus (a similar but less stable plant product to derris), for the control of mosquitoes, flies, and lice, and for agricultural use, created acute shortages just before the last war and until D.D.T. and Gammexane were fully developed. A reasonable substitute for pyrethrum was found in dodecyl and isobornyl thiocyanates, and served in many of the insect powders used during the war. However, the greatest advances in insect pest control came with the development of the D.D.T. and Gammexane insecticides.

D.D.T. is prepared by condensing chlorobenzene with chloral or its hydrate, or alcoholate, in the presence of acid. Its chemical name is 1:1:1:trichloro-2:2:di-*p*-chlorophenylethane. Because of the great advances possible in pest control, made possible by the development of D.D.T. and other new contact insecticides, the recent literature on the subject is voluminous. Of particular importance are the official publication of the Ministry of Supply (1) in England in 1946, and several by the U.S. Department of Agriculture (2) at about the same time. Perhaps the best book on the subject is that by West and Campbell, mentioned under "Literature" on page 17. D.D.T. may be used as a powder, alone or mixed with other powders such as pyrethrum or derris, in solution in organic solvents, or as a spray, or as an aerosol. D.D.T. is particularly effective against bed bugs and body lice, and the success achieved by its use for the troops during 1939–45 war was in marked contrast to the failure of insecticides for this purpose in the 1914–18 war. For the first time in history, the use of an insecticide stopped an epidemic of typhus at the end of the last war. This was in Naples, where the civilian population was ravaged by typhus, but the British army was completely protected by the use of **A.L. 63,** which contained naphthalene and derris. The American powder **M.Y.L.** (which contained pyrethrins activated by isobutylundecenoamide) was at first used, and served to check the epidemic, but D.D.T. was used at the peak, and its use completely extinguished the epidemic.(3) The louse-ridden German concentration camps were also cleared by the use of power-driven dust guns, using mixtures containing 10 per cent. of D.D.T. It is now generally recognised that some pests are unaffected by D.D.T., including aphides, mites, and the cotton boll weevil. Care is needed in its use to prevent the destruction of beneficial insects, such as bees.

Gammexane.—This is a trade name for the γ-isomer of benzene hexachloride (1:2:3:4:5:6-hexachlorocyclohexane). Gammexane was first used as an insecticide during the last war, but its wide range of application and value were not made known until 1945.⁽⁴⁾ It is generally similar in use and effect to D.D.T., but it is somewhat faster and the effect may not be so lasting. However, it is extremely effective against certain pests not controlled effectively by D.D.T., such as locusts, cotton boll weevil, and mites. Both insecticides can be used effectively against animal pests such as lice, generally, sheep ked, sheep tick, dog and cattle ticks, blowfly and hornfly, whilst Gammexane is effective against scab mites and sarcoptic scabies. High-pressure spraying of cattle against hornfly and mechanical powder dusting of lambs against keds are now practised.⁽⁵⁾

Phosphoryl esters are amongst the latest selective insecticides and are particularly effective against sap-sucking insects such as the greenfly, mealy bugs, scale insects, and thrips. They do not harm the ladybirds that feed on greenfly and, when used in dilute solution, may be used as a spray for plants at any time of the year without doing harm. Although poisonous, these phosphoryl esters are easily hydrolysed, and their toxicity is lost within about twenty-four hours of spraying. They are compatible with D.D.T., chlordane, and Gammexane formulations, and with neutral copper sprays and wettable sulphurs. They are not compatible with alkaline materials such as lime sulphur and Bordeaux mixture. The two most common insecticides of this type are:

HETP, or hexaethyl tetraphosphate, and **TEPP,** (Nifos-T.) or tetraethyl pyrophosphate. Both may be applied in dilute solution, from .03 per cent. to .05 per cent. strength, or as aerosols. It is usual to add a wetting agent to a solution in water, or an emulsifying agent when a solution in an organic solvent is first made. All species of aphides are killed by these insecticides, and amongst the mites killed are the red spider, citrus red mite, two-spotted mite, and bryobia mite.

Insecticides are now being developed intensively in many countries based upon the above newer products, but the older insecticides and fungicides, described earlier, are still used in large quantities, and will probably continue to be so used for many years.

REFERENCES

(1) Ministry of Supply, "Some Properties and Applications of D.D.T." London, 1946.
(2) U.S. Dept. Agric., Misc. Pub. 606 (1946); R. C. Roark, *ibid*, E-631 (1944); E-660 (1945).
(3) H. J. Craufurd-Benson, *Brit. Med. J.*, **1**, 579, 710 (1946).
(4) R. E. Slade, *Chem. and Ind.*, 314 (1945).
(5) J. G. Matthyse, *J. Econ. Entomol.*, **38**, 285 (1945); **39**, 62 (1946).
(6) G. F. Ludvik and G. C. Decker, *J. Econ. Entomology*, **40**, 97 (1947).

SECTION LIV

ARTIFICIAL MANURES

By Arthur S. Carlos, B.Sc. (Lond.), A.I.C.
Revised by Wilfrid Francis

LITERATURE

F. E. Bear.—"Theory and Practice in the Use of Fertilisers." London, 1938.
—— "Soils and Fertilisers." London, 1942.
Sir E. J. Russell.—"Fertilisers in Modern Agriculture." London, 1939.
—— "Students' Book on Soils and Manure." London, 1940.
G. H. Collings.—"Commercial Fertilisers."
P. Parrish and A. Ogilvie.—"Calcium Superphosphate and Compound Fertilisers." London, 1946.
—— "Artificial Fertilisers." London.
S. H. Collins.—"Chemical Fertilisers." London.
G. Taylor.—"The Fertilisers and Feeding Stuffs Act and some Analytical Implications." 33rd Streatfeild Memorial Lecture, R.I.C. London, 1948.
B.I.O.S./JAP./PR./1164.—Fertilisers in Japan" (1947).
B.I.O.S. 1443.—"The German Nitrogenous Fertiliser Industry in Western Zones" (1947).
B.I.O.S. 1557.—"The Manufacture of Technical Phosphates in Western Germany" (1947).
J. S. Remington and W. Francis.—"Manure and Fertilizer Notebook." London, 1953.

In general, plants obtain their carbon (as carbon dioxide) from the air, water from rain, and nitrogen (as ammonia or combined nitric acid) from the soil. Certain plants (*i.e.*, legumes) are able to assimilate free nitrogen from the air.

In addition to these three chief substances other nutriments are required, such as are found in the ash of most plants. They are :—

Potash, K_2O.
Lime, CaO.
Iron oxide, Fe_2O_3.
Sulphuric acid, H_2SO_4.
Hydrochloric acid, HCl.
(Sometimes soda, Na_2O.)
Magnesia, MgO.
Silica, SiO_2.
Phosphoric acid, H_3PO_4.
Boron, Manganese, Zinc.

Most of these are present in sufficient quantities in virgin soil, but their stock can very easily be used up, especially if the soil is poor, and often at a greater rate than that at which it is replenished ; consequently manures have to be put on the land in order to replace, in the soil, the constituents removed by the plants.

In all manures the active constituents should be easily assimilable by the plants. In other words, the manure should decompose fairly rapidly, and also the chief constituents should be soluble in water or very dilute acid.

I. PHOSPHATIC MANURES

Natural Phosphates.—Extensive deposits of natural phosphates occur in various parts of the world. The harder of these raw phosphates, even in the finest milled condition, are of very little manurial value, because they are only very slowly soluble in water, and hence plants can only make use of them very slowly. The softer minerals, if sufficiently finely ground, have an appreciable but limited value for direct application to the soil.

The chief deposits are :—

(i.) **Coprolites.**—This was the first deposit to be used as a manure. It occurs in the Jurassic Strata and Suffolk Crag, particularly in Cambridge, Gloucestershire, and Bedfordshire, and consists

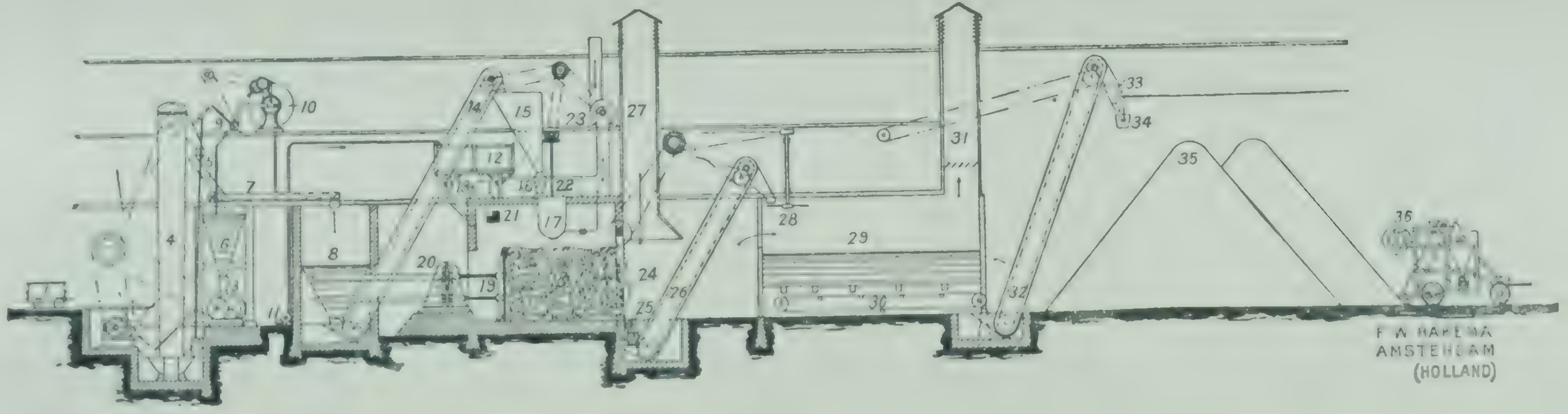


FIG. 1.—Complete Superphosphate Fertiliser Plant (see p. 31).

1. **Tip waggon for raw phosphate.**
2. [illegible]
3. **Mill.**
4. **Elevator.**
5. [illegible]
6. **Feed hopper for mill.**
7. **Worm conveyer for ground phosphate.**
8. **Store bin for fine phosphate.**
9. **Exhaust fan.**
10. Dust collector.
10a. Dust collecting pipes.
11. Centrifugal pump for acid.
12. Acid store tank.
13. Acid measuring tank.
14. Fine phosphate elevator.
15. Fine phosphate feed hopper.
16. Special weighing machine.
17. Acid and phosphate mixer.
18. "Svenska" den-excavator.
19. Piston.
20. Worm-wheel gearing.
21. Ventilation.
22. Condenser flues.
23. Exhaust fan.
24. Crumbling arrangement.
25. Superphosphate conveyer.
26. Superphosphate elevator.
27. Ventilation.
28. Slicing (rasping) machine.
29. Store silo for sliced super.
30. Belt conveyer.
31. Outlet flue from store silo.
32. Superphosphate elevator.
33. Small feed hopper.
34. Mono rail system.
35. Finished superphosphate in store.
36. Portable bagging and weighing machine.

of the excrement of Saurians metamorphosed to tricalcium phosphate. Coprolites usually contain about 25 per cent. phosphoric oxide (P_2O_5) and about 42 per cent. lime (CaO). English coprolites are no longer in use.

(ii.) **Sandy Phosphates.**—These deposits occur in Belgium, and in France on the Somme.

(iii.) **African Phosphates** are deposits found in the north of Africa. The beds in Tunis (Algerian phosphate) are extremely important, and contain about 30 per cent. P_2O_5 and 48 per cent. lime.

(iv.) **Deposits in Florida, Tennessee, and South Carolina.**—The composition of Florida phosphate is on the average 35 per cent. P_2O_5, 2.5 per cent. Fe_2O_3 and Al_2O_3, and 45 per cent. CaO.

(v.) **Christmas Island Phosphates**, from Christmas Island, south of Java, where there is estimated a bed of 2½ million tons, consisting of a white phosphate, very easy to mill if sufficiently dry. Its average composition is 87 per cent. tricalcium phosphate, 0.5 per cent. iron oxide, 1 per cent. alumina, and 6 per cent. lime.

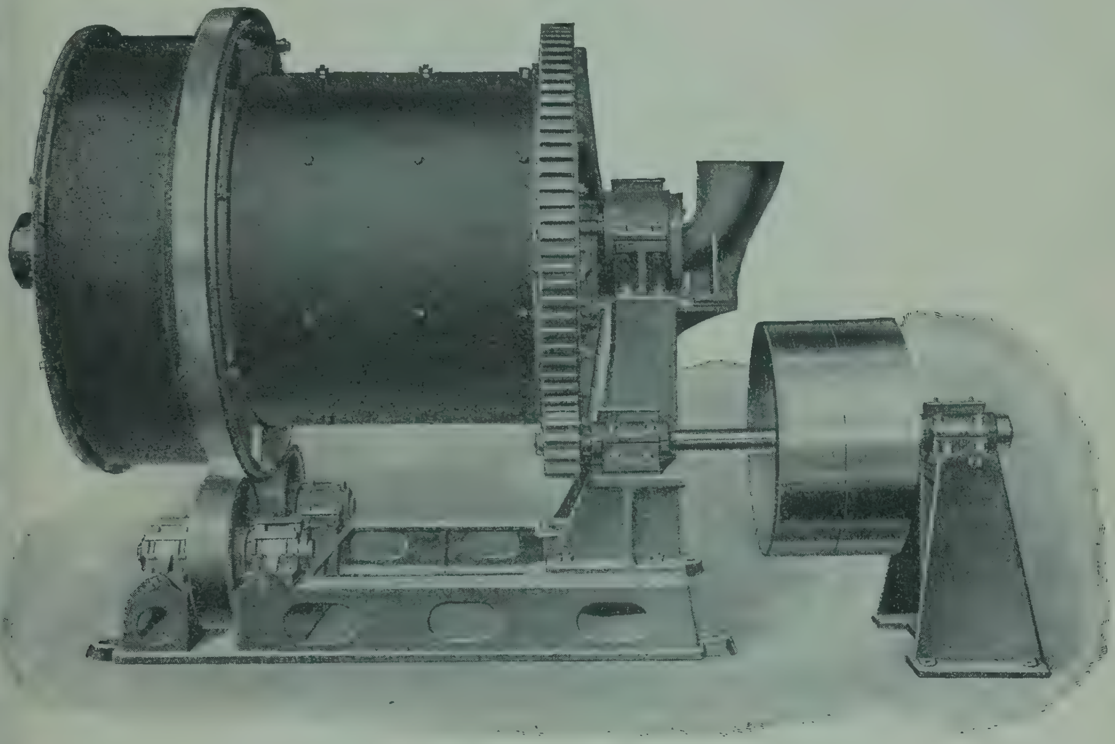


FIG. 2.—Abbé Ball Mill.
(*The Abbé Engineering Co., New York.*)

(vi.) **Pacific Phosphate.**—There are two extensive deposits of this phosphate which are now being worked to a very large extent.

(*a*) **Ocean Phosphate** from Ocean Island (British), in the Gilbert Group. This is a very extensive deposit of mineralised guano, the excrement of sea birds, which has accumulated for thousands of years. The phosphate is light to dark brown in colour, crushes well, and is fairly easily assimilable by plants. It contains about 85 per cent. acid calcium phosphate, 0.5 per cent. iron oxide and alumina, and 5 per cent. calcium carbonate.

(*b*) **Deposit at Nauru Island** (Pleasant Island), belonging to the Marshall Islands. This deposit is exactly similar to ocean phosphate.

(vii.) **Further Deposits.**—In the States of Idaho, Utah, and Wyoming new deposits have been discovered. These are estimated at least at 100 million tons.

Great deposits also occur at Angaur Island (Paulau), west of Caroline Islands, where about 2½ million tons of an 80 per cent. phosphate are said to exist. The deposits at the Island of Makatu in the Tuamotu archipelago, have not yet been fully investigated.

The phosphate in all these deposits exists chiefly as tricalcium phosphate, and appears to have arisen from the action of phosphoric acid (of organic origin) on calcium carbonate. Phosphate in this form is very slightly soluble in water, so that it is necessary to convert it into a soluble form, such as superphosphate, before it is of much use as a manure. The first step is to crush the mineral phosphate, then grind and separate the fine powder. This process of milling has been carried on for a long time in a wrong manner by using mills that are not suitable for the purpose.

Crushing.—The raw material should be first crushed so as to reduce the larger lumps to a convenient size for the grinding mill.

This is done in special machines, such as the **Roll Jaw Rock Crusher** or the **Rotary "Open Door" Fine Crusher**, supplied by the Sturtevant Engineering Co. Ltd., of London, and which the writer can recommend. Similar machines are described under the **Calcareous Cement Industry, p. 92,** to which the reader is referred for a description.

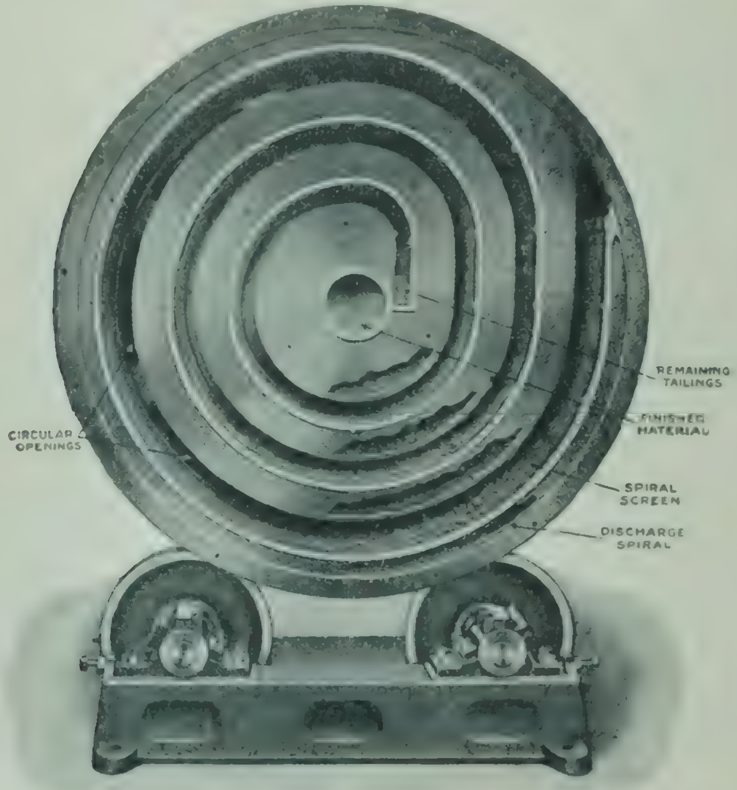


FIG. 3.—Abbé Ball Mill—Spiral Screen (open).

(*Abbé Engineering Co., New York.*)

Grinding.—After the phosphate has been crushed it is transferred to a suitable mill for grinding or disintegrating.

The best mills in use at present are:—

(1) **Ball Mills.**—The Abbé Ball Mill, manufactured by the Abbé Engineering Co., New York (see Figs. 2 and 3), consists of a rotating drum-like cylinder containing steel balls, and covered inside with steel step-like plates. The material to be ground enters this chamber through a hole at the end (seen on the right, Fig. 2).

The crushing is performed by the balls falling from one step on to the next. To the end of the chamber is bolted a patent spiral discharge, and screening spiral. The spiral screen consists of a number of convolutes of diminishing diameter as they approach the centre.

The crushed material passes into the screen on its largest convolute (see Fig. 3), and after sifting over the whole length of the spiral, the remaining tailings are delivered, by means of a conveyer at the centre, to the opposite end of the grinding chamber. The various convolutions of the screen are surrounded by a discharge spiral which runs the full length of the screen spiral, and conveys the finished product to the discharge at the centre of the end of the machine.

(2) **Tube Mills.**—These are essentially mills for fine grinding. A typical mill consists of a long tube of steel plates (up to 30 ft. long and 6 ft. diameter), containing a number of flint or steel balls, and revolved by suitable gear. The mill is capable of being used for either wet or dry grinding, and this is effected solely by the flint pebbles or steel balls rubbing against each other

and the side of the tube. The feed is placed at one end, and the outlet at the other. Fig. 4 shows a tube mill capable of turning out about 4·7 tons of very fine finished powder per hour. The material delivered to the mill should be pulverised to about $\frac{1}{2}$-$\frac{3}{4}$ in. cubes, and the final product separated, the coarse particles being returned to the mill. One of the great advantages of such mills is the simplicity in construction; no sieves are required, and hence there is freedom from breakdown.

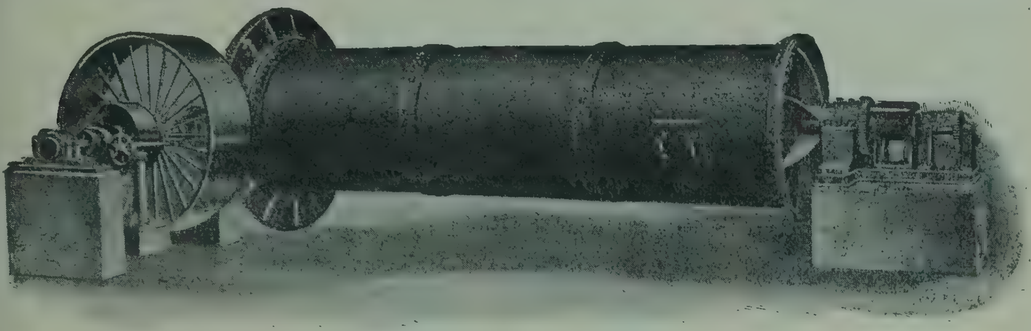


Fig. 4.—Tube Mill.
(*Edgar Allen & Co. Ltd., Sheffield.*)

(3) **Ring-Roll Mills.**—By far the best mills of this type are those patented by the Sturtevant Engineering Co. Ltd., London. These essentially consist of a heavy steel anvil ring, concave on the inside (see Fig. 5), and revolved by a horizontal shaft. Three, so-called, hammer rolls are pressed against the ring with enormous force by springs, and a lever arrangement on the axles. These rolls are convex, and work free. The revolving ring drives all three rolls by means of an inch layer of centrifugally held material seen at R (Fig. 5).

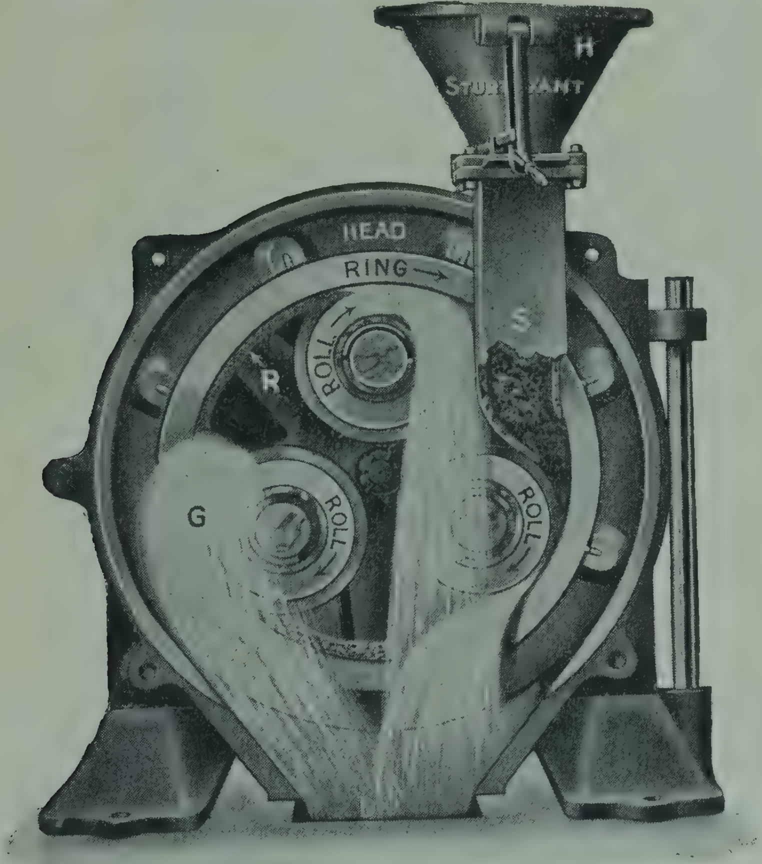


Fig. 5.—Ring-Roll Mill (section).
(*Sturtevant Engineering Co. Ltd., London.*)

The feed enters the hopper at H, and is delivered by the spout S at the centre of the concave surface of the ring, where it is strongly held by centrifugal force (seen at R), until the ground rock is crushed off on both sides of the ring (as at G), and discharged at D.

These mills are very durable, and give a large output, using little power. They have replaced many other grinding mills.

(4) **Roll Mills.**—The most efficient mill of this pattern is the Bradley three-roll mill (Fig. 6) manufactured by the Bradley Pulveriser Co., London. In the figure the upper and part of the lower shield are removed in order to show the working parts. Three rolls, free to move, are supported in a pendulum fashion from a central vertical shaft, and hang inside a fixed annular ring or die. When the shaft revolves, the rolls tend to rise by centrifugal action and crush against the ring. The crushing power varies with the speed of the shaft. The material to be ground is fed to a central hopper surrounding the shaft, and is distributed continuously on to the ring directly in front of the three advancing rolls by long spouts (seen in Fig. 6); hence the material is fed exactly in the place where it is to be ground. This is a slow-running mill, and all the working parts are easily accessible.

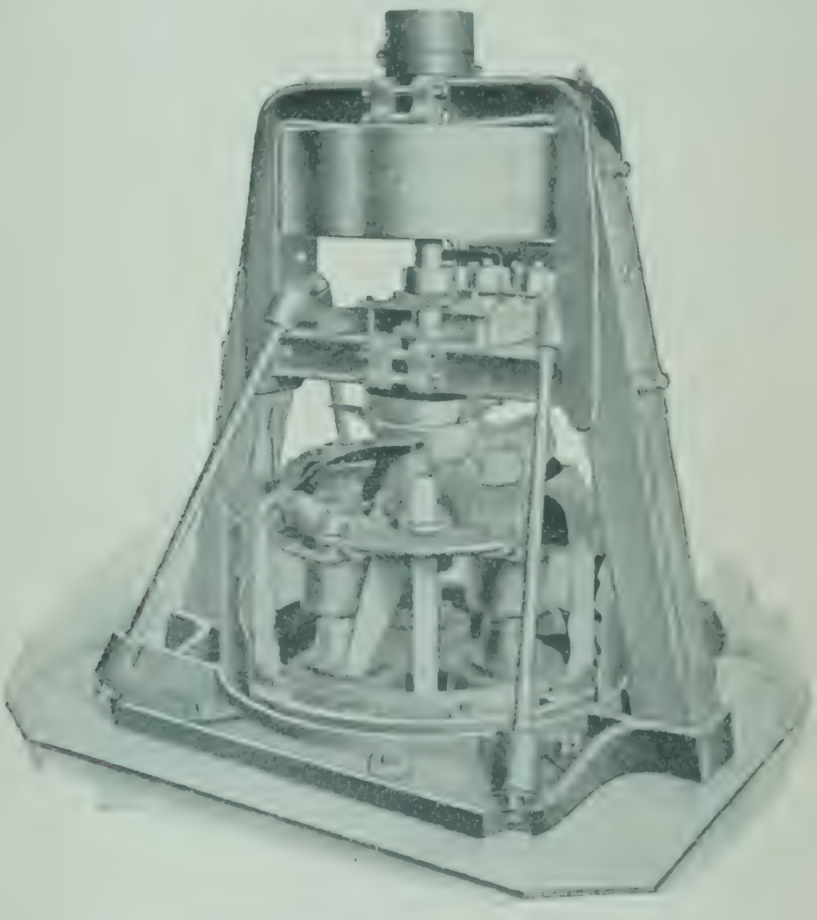


FIG. 6.—Bradley Three-Roll Mill.

(*Bradley Pulveriser Co., London.*)

The output of the Bradley three-roll mill, with phosphate rock, is as follows:—

On Florida high grade rock—2½-3 tons per hour; on Florida land pebble phosphate—3½-4 tons per hour, both ground to a fineness of 80-85 per cent. to pass a 100 mesh sieve (= 10,000 holes per square inch). A higher output up to 6 tons per hour is obtained with softer phosphate rocks.

(5) **Disintegrating Machines.**—In these machines disintegration is brought about by blows which are either on the supported or the unsupported particles of the material.

Mills of the first type are mostly stamp mills, and are chiefly used in the mining industry and districts. A very good disintegrator of the second type is "Carter's" Disintegrator, supplied by J. Harrison Carter, Dunstable, and seen in section in Fig. 7. It consists of a circular chamber lined with cast-iron plates which have grooved or toothed surfaces, F and G. The lower half of the circumference of the chamber is formed of screens H from [illegible] in. mesh according to the required fineness of the finished product.

A strong spindle A passes through the centre of the chamber, and carries four or six iron beaters C attached to a very strong steel disc B. These beaters are replaceable, and run close to the inner circumference of the grinding chamber, covering its whole width. The material to be ground is fed as near as possible to the periphery of the chamber, and there it meets the beaters while they are travelling at a high speed of 15,000-20,000 ft. per minute. The material is thus beaten and driven against the lining. As the particles become sufficiently fine they pass through the screens into the chamber below, the coarse particles being again operated on by the beaters, and finally reduced.

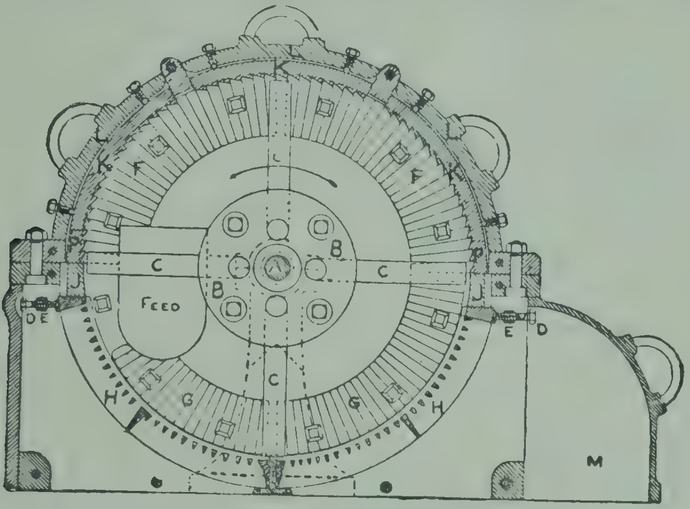


FIG. 7.—Section of Carter's Disintegrator.
(J. Harrison Carter, Dunstable.)

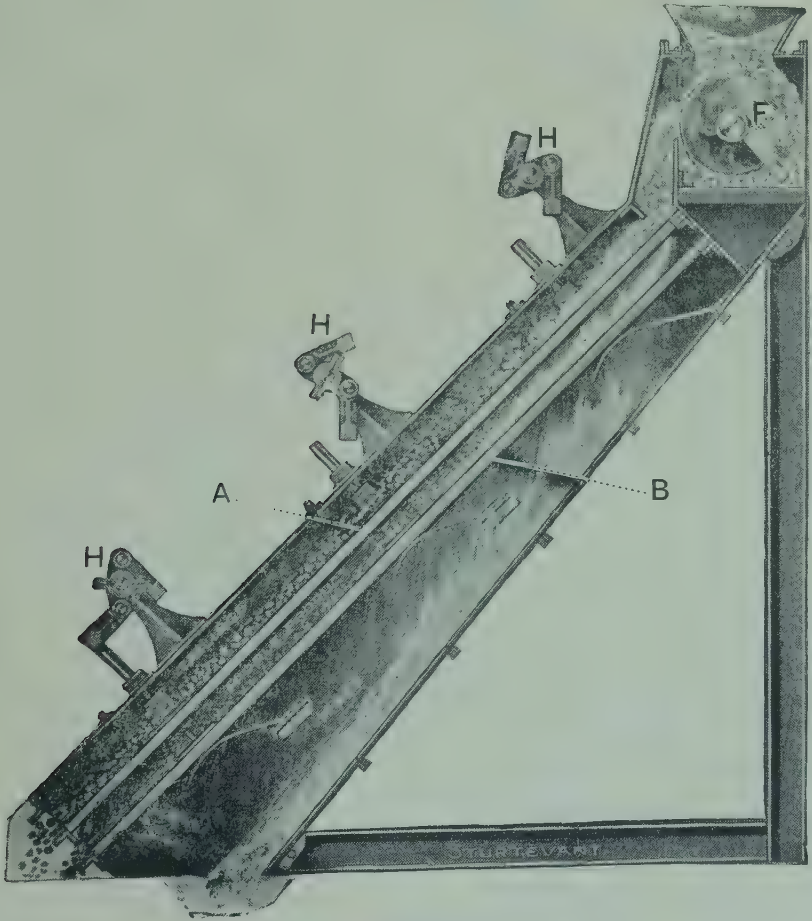


FIG. 8.—Sturtevant-Newaygo Separator.
(Sturtevant Engineering Co. Ltd., London.

Separators.—These are used to separate the fine ground phosphate.

(1) **Screen Separators.**—An excellent machine of this type is the Sturtevant-Newaygo Patent Separator (Sturtevant Engineering Co. Ltd., London), seen in the diagram (Fig. 8). The screens A and B are made of stretched wire cloth, and are subjected to very light and rapid blows from the hammers H, which cause the mesh to keep in constant vibration. These hammers are driven by gearing to the revolving feed F placed right along the top of the screen.

(2) **Air Separators** (see Fig. 9).—This type of separator consists of a funnel-shaped iron vessel having two casings H and G separated from each other. The material is fed from the hopper K on to the disc A, rotated by the pulley B. The lower part of the hopper, as well as the fan F, are driven by the pulley C.

The material is spread out in a fine stream by the plate A towards a fixed hood G directly below the fan. Here there is a strong current of air, produced by the fan F and coming through the slits E. This air stream carries the smaller particles forward into the chamber G, while the larger particles, too heavy to be carried up by the air, strike against G, and fall into the casing H. The degree of fineness of the finished product can be regulated by the speed of the fan.

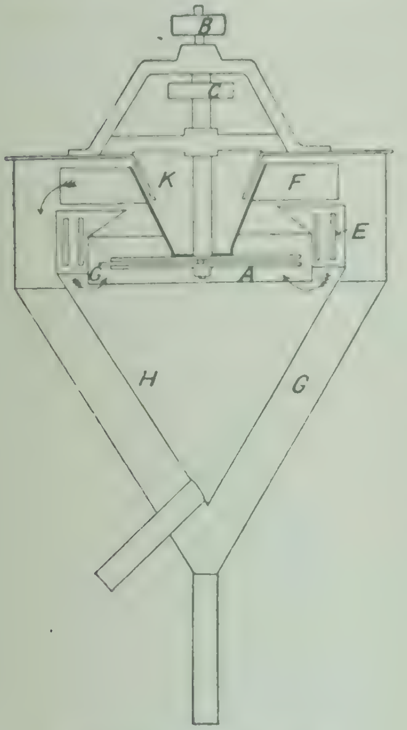


FIG. 9.—Section of an Air Separator.

Complete Plant for the Treatment of Phosphate Rock

Fig. 10 shows a suitable plant for crushing, grinding, and screening phosphates, supplied by the Sturtevant Engineering Co. Ltd., London.

The material is first crushed in the **roll-jaw fine crusher** A, and falls into the "crushed rock bin" D, from which it passes, by gravity, to the **ring-roll mill** C, where the grinding takes place.

The ground material is next elevated to the Sturtevant patent separator B, where it is screened, the finely milled portion passes into the "fine rock bin" E, while the tailings pass on to the bin D for further treatment.

Superphosphate.—After milling, the powdered phosphate is treated with sulphuric acid in order to convert the insoluble tricalcium phosphate into soluble monocalcium phosphate or superphosphate :—

$$Ca_3(PO_4)_2 + 2H_2SO_4\,[+ 6H_2O] \rightarrow 2CaSO_4 + CaH_4(PO_4)2\,[+ 6H_2O].$$

(Tricalcium phosphate.) (Sulphuric acid.) (Calcium sulphate.) (Monocalcium phosphate.)

This formula does not represent exactly the chemical change that takes place. If a smaller amount of acid is used, insoluble dicalcium phosphate is formed, as in the following equation :—

$$Ca_3(PO_4)_2 + H_2SO_4 \rightarrow CaSO_4 + Ca_2H_2(PO_4)_2$$

Similarly, if a large amount of acid is added, the following change takes place, phosphoric acid being liberated :—

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4.$$

In the manufacture of superphosphate care must be taken to use the requisite amount of acid, because if it is present in large excess a sticky product will be the result, and this is liable to be reverted into insoluble calcium phosphate or "Precipitated" phosphate. Reversion also takes place if superphosphate is kept for a long time :—

$$CaH_4(PO_4)_2 \rightarrow CaHPO_4 + H_3PO_4.$$

Iron oxide and alumina may also bring about this change, hence care must be taken in mixing superphosphates with other manures.

Process of Manufacture.—Chamber acid of 1.55-1.60 sp. gr. is chiefly used; the quantity must be so adjusted that to one molecule of calcium phosphate there are rather more than two of acid; also sufficient acid must be added to convert the excess of lime (present as calcium carbonate and calcium fluoride) as well as the iron and aluminium oxides into sulphates :—

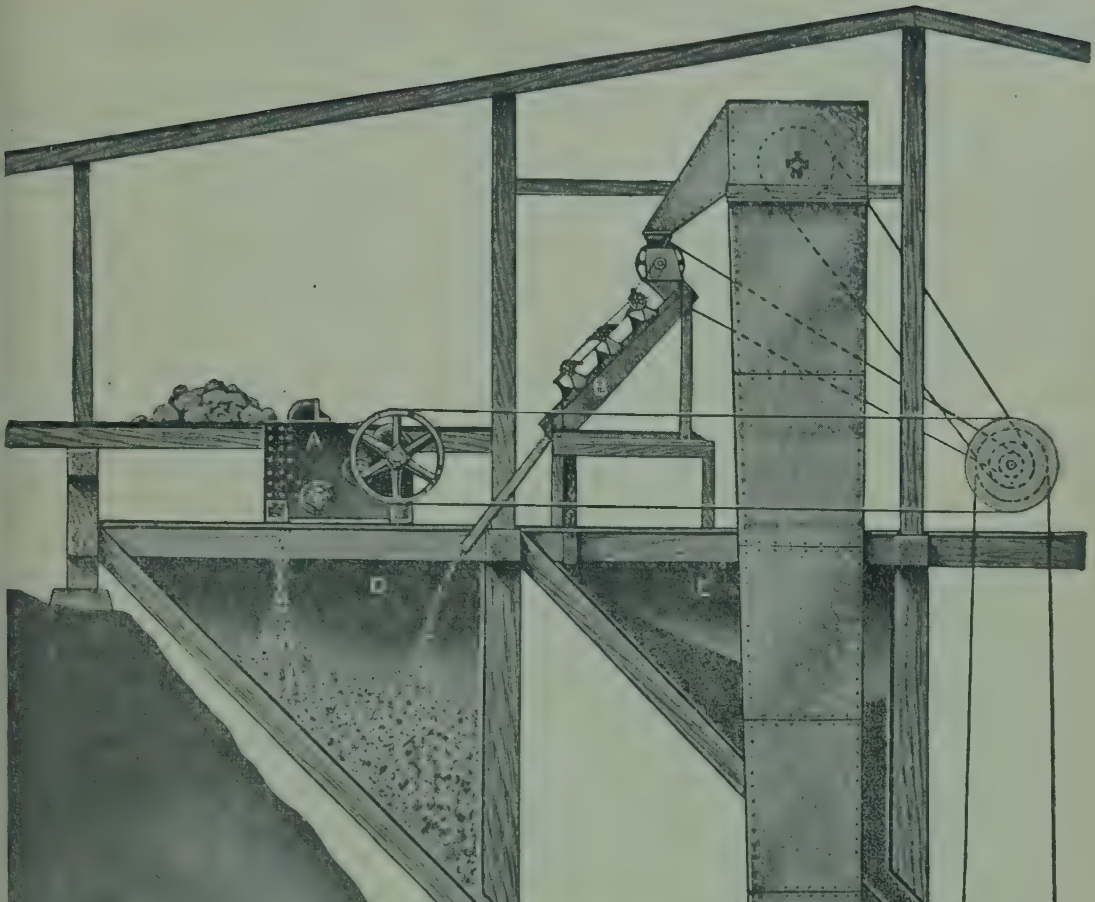


FIG. 10.—Phosphate Unit.

(*Sturtevant Engineering Co. Ltd., London.*)

It is usual to effect this decomposition according to analysis. A general analysis is made of each batch of phosphate to be treated, and the calculated amount of acid, plus about 5 per cent., is added, *i.e.*, 105 pts. of chamber acid per 100 pts. of ground phosphate.

The acid must be used cold: sufficient heat will be evolved during the reaction to effect the decomposition. According to French Patent, 419,716, 1910, a little nitric acid added to the sulphuric acid accelerates the decomposition.

Fig. 11 shows the **Milch patent superphosphate den** supplied by W. J. Fraser & Co., of Dagenham, Essex.

The various grades of finely milled phosphates are conveyed from storage bins to a weighing machine which empties a weighed quantity of phosphate into the mixer R (Fig. 11); next the requisite amount of acid is measured into the mixer by another machine working automatically in conjunction with the first. The mixture is now well stirred, and by opening a valve at the bottom of the mixer the contents fall into the chamber or den D where the action completes itself.

This chamber consists of a large cylinder D made of iron plates and mounted on running wheels, so that it can remain inside the large closed brick chamber C or be withdrawn. On either side of the cylinder D there is a long screwed shaft S, which works in threads fixed on the side of the cylinder; by rotating these shafts, the cylinder D can be slowly drawn out of the chamber C.

There is an opening all along the top and bottom of the cylinder D. The bottom opening is closed by means of heavy wooden doors during the process of filling. The back end of the cylinder consists of a permanent steel plate, while the front is left open and closed by a wooden door bolted on.

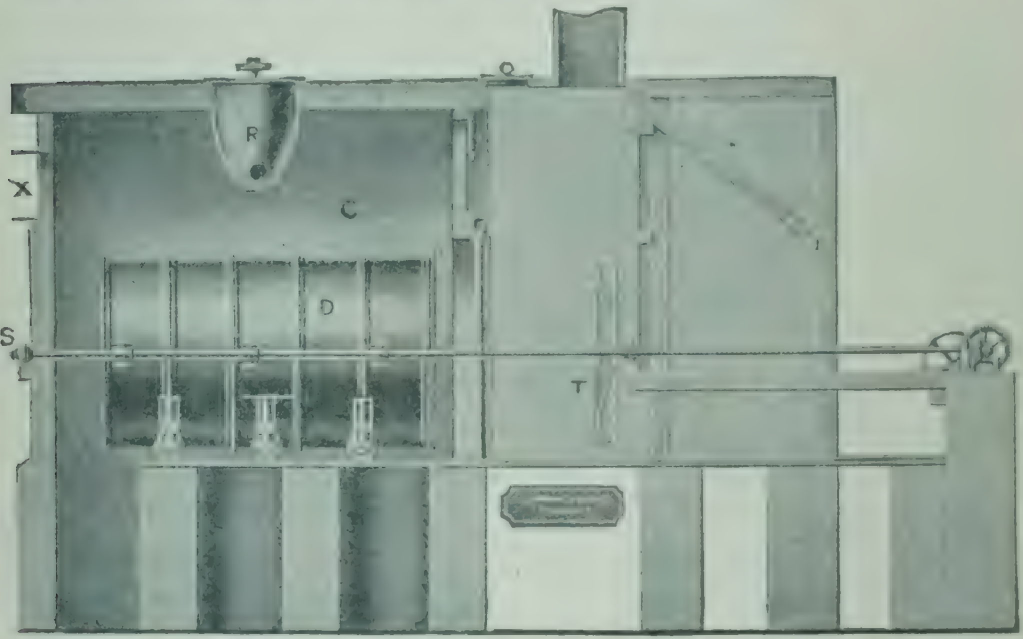


FIG. 11.—Milch Patent Superphosphate Den.
(*W. J. Fraser & Co., Dagenham.*)

After the cylinder D has received its charge of mixed acid and phosphate (15-40 tons according to size), it is allowed to stand for a short time inside the brick chamber C; sufficient heat is developed to carry out the change into superphosphate.

The acid gases which escape both at this stage and in the subsequent excavation of the superphosphate are carried away by a ventilating shaft X, which is connected with a fan to absorption towers. Modern arrangements are described in Vol. I., p. 417, under **The Hydrofluoric Acid Industry**.

Next the front door of D is removed, and the bottom doors dropped on their hinges, and the work of excavating the superphosphate from D is now commenced.

Many difficulties have been experienced in the manner of excavating the superphosphate from the den D: firstly, the material must be cut away without any rubbing action, which spoils its physical condition; secondly, there must be no undue pressure which might spoil its chemical condition; and thirdly, the difficulty from the corrosive action of the chemicals and gases must be overcome.

In the **Milch chamber** and most other dens the excavating is carried out automatically. A revolving knife T of rather less diameter than the cylinder D is arranged on a third shaft and fixed in front of the cylinder (as shown).

When the machinery is started the knife T is caused to rotate about fifty times per minute; simultaneously the screw shafts rotate which slowly draw the cylinder D towards the knife T. The material in the drum is thus shaved off to a very fine powder which falls inside the cylinder and drops through the bottom opening on a special conveyer by which it is taken to the storage sheds.

The power needed for such a plant is comparatively small, and the output per day amounts to about 160 tons.

Fig. 1 shows in detail an excellent up-to-date plant (made by Bakema, of Amsterdam) for the manufacture of superphosphate.

In some cases the chamber is placed vertically and the lower end removed for emptying.

The product, **superphosphate of lime,** is generally called "**superphosphate**" or "**mineral superphosphate.**" The strength varies according to the material used, and is judged by the amount of phosphate soluble in water, and in a 2 per cent. citric acid solution. Usually superphosphates contain 25-28 per cent. of soluble phosphate, but some samples contain a much higher percentage.

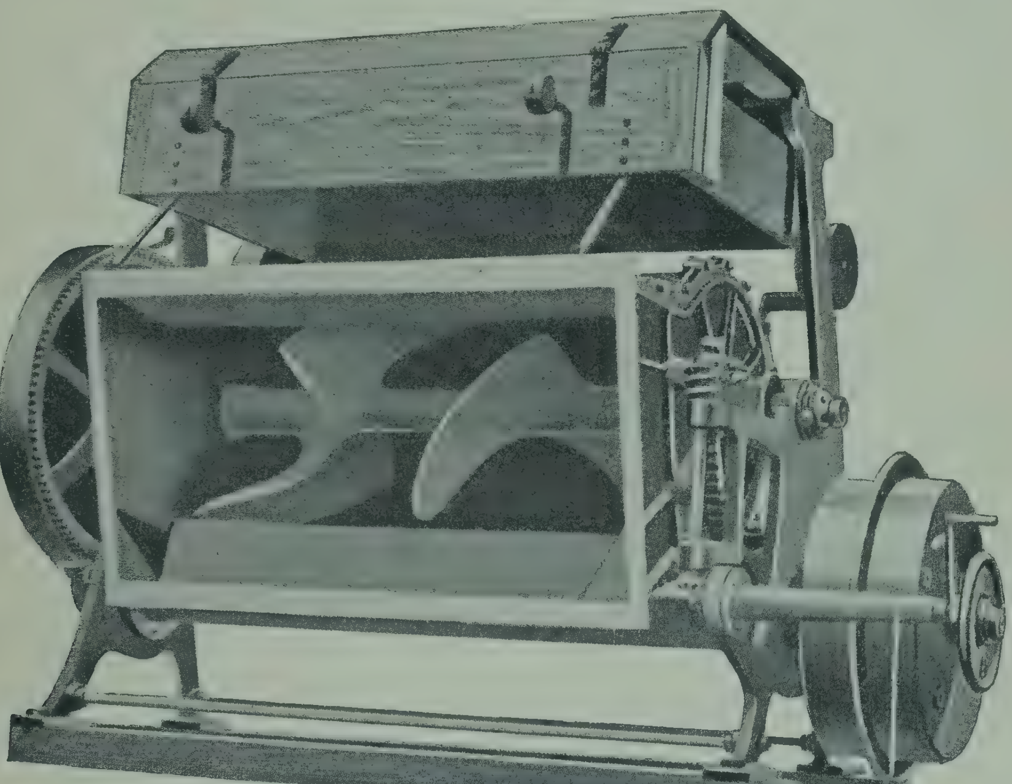


FIG. 12.—"Single-Blade Mixing Machine."
(Baker-Perkins Ltd., Peterborough.)

Superphosphate should be in a friable and dry condition or else it will clog the drills when used for manuring. The colour of the sample is not a criterion as to the quality.

Basic Superphosphate.—This contains excess of lime and is made by neutralising the excess of acid in superphosphate by lime. According to English Patent, 3,327, 1912, if superphosphate is heated to about 825° C. the calcium sulphate is decomposed, and sulphuric acid is driven off, forming lime. Water also passes off, forming a basic superphosphate containing about 40 per cent. of lime.

Double Superphosphate contains some 45 per cent. water-soluble phosphoric acid, and is made as follows: Phosphoric acid solution is first obtained by the action of sulphuric acid on natural phosphates, and filtering off the gypsum formed.

The solution is now evaporated in covered pans, and stirred with the requisite quantity of phosphate meal, then drying the double superphosphate which is formed.

Phosphoric acid prepared in this manner is also used for making potassium, sodium, and ammonium phosphates.

Dissolved or Vitriolised Raw Bones.—Manures of this type are prepared by treating crushed bones with sulphuric acid, which converts the calcium phosphates into an acid phosphate.

A suitable mixer, and one that will resist the action of the acid, is made by Baker-Perkins Ltd., of Peterborough. This is shown in Fig. 12, tilted to empty the contents.

Raw unsteamed bones should be used in the manufacture, and excess of acid must be avoided as it forms a pasty mass.

In order to obtain a good product the bone meal should be in a fine condition, and the mixing well carried out. Dissolved bone meal usually contains 30 35 per cent. of total phosphate and nitrogen equivalent to 3-3.5 per cent. ammonia. If steamed bones are used the product will not be so rich in nitrogen.

Analyses of various raw and steamed bone meal (according to J. Richardson, York) are as follows:—

	Raw Bone Meal.	Steamed Bone Meal.
Moisture - - - - - - - -	9.10	6.30
* Organic matter - - - - - - -	35.96	12.90
† Phosphoric acid - - - - - - -	22.00	32.10
Lime - - - - - - - - -	20.20	41.97
Magnesia, alkalis, etc. - - - - -	2.74	6.58
Insoluble siliceous matter - - - -	1.00	0.15
	100.00	100.00
* Containing nitrogen - - - - -	4.27	1.38
Equivalent to ammonia - - - - -	5.18	1.67
† Equal to tribasic calcium phosphate -	48.04	70.07

Dissolved Bone Compounds.—These are made by mixing dissolved bone meal with water-soluble mineral phosphates. Sometimes other substances, such as dried blood, guano, etc., are added to the bones before dissolving in the acid.

The composition of such manures naturally varies: a good quality sample contains about 30 per cent. total phosphates, of which 20 per cent. is soluble in water, and 1.25 per cent. nitrogen (equal to 1.5 per cent. ammonia). A poorer sample may only contain nitrogen up to about 1 per cent. ammonia.

Basic Slag.—(Otherwise known as basic cinder, basic phosphate, Thomas slag, Thomas meal, or Thomas phosphate.)

This is a by-product of the Thomas-Gilchrist process for the Bessemer conversion of phosphatic pig iron into steel. The phosphorus, at the high temperature of the molten iron, is converted into tetra-calcium phosphate by combining with the coating of lime in the converter; this phosphate, unlike tri-calcium phosphate, is soluble in citric acid solution.

The actual percentage of phosphate in the slag varies considerably; medium grade slag contains about 30 per cent., and the best grade about 40 per cent. of phosphate calculated as $Ca_3P_2O_8$. The same tetra-phosphate, under the name of Wiborgh-phosphate, is formed in Germany by heating mineral phosphates with soda.

Basic slag is a very heavy material, and when finely ground forms an excellent manure, the phosphorus being more readily available than in the case of natural phosphates.

The preparation of the slag as a manure simply consists in fine crushing and separating.

This is usually carried out at the iron works. Some of the most suitable mills used in this work are ball or ball-tube mills (see p. 24), whilst air separation is the best. On the average about 80 per cent. of the slag should pass through a sieve of 10,000 meshes to the square inch. According to English Patent, 63, 1902, Thomas slag is converted into a powder by the action of steam.

The value of the meal depends on the percentage of citric-soluble phosphoric acid it contains. In good slag 80-90 per cent. of the total phosphoric acid should be soluble in a 2 per cent. citric acid solution.

Two typical analyses of basic slag, as given by J. Richardson & Co., are as follows:—

	30 °/. Grade.	39 °/. Grade.
Silica	12.60	8.10
Peroxide of iron	10.87	10.20
Protoxide of iron	7.01	8.54
Protoxide of manganese	6.19	5.34
Lime	44.53	45.42
Magnesia	4.12	3.63
Sulphur	0.27	0.41
Phosphoric acid	14.41	18.36
	100.00	100.00

Basic slag is suitable for clay and peaty soils, moorland, fruit, and vineyards, and generally all lands poor in phosphoric acid. The action is somewhat slower than in the case of superphosphate, but the actual cost of the phosphoric acid in the slag is about three-quarters the price of that contained in superphosphate.

The annual output of slag in the United Kingdom now amounts to some 600,000 tons, of which nearly all are used for home consumption. The Continental production alone is estimated at 3,000,000 tons, while over 2,200,000 tons are used annually in Germany.

II. PHOSPHO-NITROGENOUS MANURES

Bones.—(*a*) **Raw and unsteamed bone manure** is rich in phosphorus and fairly rich in nitrogen.

Crushing.—Bones are crushed in any suitable mill; the type usually used consists of a pair of toothed rollers between which the bones pass. Unless the bones are finely crushed they are best used on the land early in the season on account of the time taken to decompose.

Good raw bone meal contains 40-50 per cent. phosphates, and 3.5-4 per cent. nitrogen (equivalent to 4-5 per cent. ammonia). English raw bone meal generally contains 45 per cent. phosphates and 3.5 per cent. nitrogen:—

Indian bone meals have been placed on the market, and are usually slightly richer than the English varieties.

Raw bone meal is more often used for permanent pastures than for crops, on account of its slow rate of action.

(*b*) **Steamed or Degelatinised Bones.**—Crushed bones are treated with superheated steam and benzene to remove the fat and glue (for description of process, see **Martin's** "Industrial Chemistry: Organic," pp. 31 and 595). The bones after treatment contain only about 1 per cent. of the nitrogen, and after grinding are sold as "steamed bone meal":—

Another method of extraction is to soak the bones in 8 per cent. hydrochloric acid for some days. This takes out all the phosphate, which is then thrown down as dicalcium phosphate by lime; the so-called "Lime Precipitate" is citric soluble, and is an excellent manure, only it is fairly expensive.

The value of steamed bone meal is less than raw bones on account of the smaller nitrogen content; the amount of phosphates is, however, higher.

Flesh Meal (flesh guano or meat meal) is obtained from the carcasses of horses and other animals, the putrid animal refuse from slaughter-houses, garbage, etc.

Suitable plants have been designed and are in operation at various places. The refuse is placed in a sieve in an iron cylinder into which superheated steam is passed; after a few hours the meat becomes thoroughly cooked. The fat and gelatine broth drop down and are collected; the evil-smelling steam is also collected by condensation. The solid matter after straining is reduced, by pulverising, to a pulp and then conveyed to a suitable drying apparatus. The dried product is called **flesh meal** and is completely scentless: it contains 6-8 per cent. nitrogen and 6-15 per cent. phosphoric oxide.

The water or tankage that separates from the above cooking is stored in vats, heated to 170° F., and the grease removed as completely as possible; this is important, because if grease is present, it interferes with the evaporation. The liquid is now evaporated in a suitable machine, the dried product being used as a manure.

The so-called "**Fray-Bentos**" **guano** is produced in a similar manner from the residue during the manufacture of Liebig's extract of meat.

Fish Manures or Guanos.—These are largely made from the residue and offal from fisheries, and sometimes (as in America) from whole fish.

The fish scrap is carried in a continuous stream to the **cooker** or **digester** (Fig. 13 (A)).

This consists of a horizontal cylinder to one end of which is fitted a mechanical feeder. A long hollow steel shaft, capable of being rotated, passes through the cylinder, and carries a special spiral conveyer which, by rotation, continually moves the material through the cooker. The shaft is also provided with hollow radial arms, and pierced with numerous holes.

The fish scrap is thoroughly disintegrated by the rotating of the shaft, and cooked in a few minutes by the steam which passes through the shaft and arms.

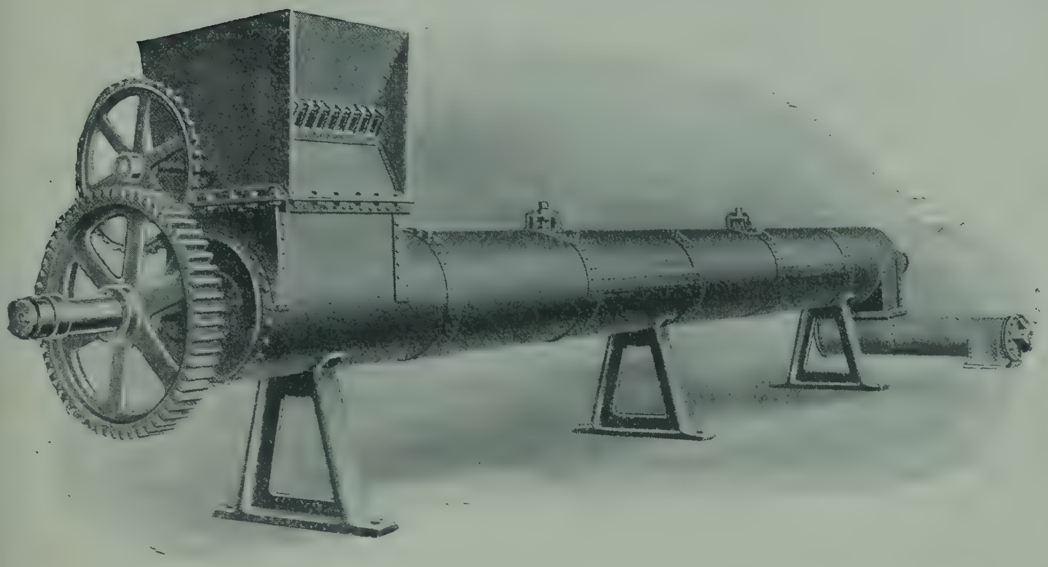
When the material reaches the other end of the cylinder, it is automatically conveyed to the **press** (Fig. 13 (B)).

The central rotating hollow shaft of the press carries a tapering pressing screw which revolves in a similar conical steel casing. The wet material is fed by means of a mechanical device, and discharged at the smaller end of the machine thoroughly pressed. The pressure on the material is regulated by the size of the opening at the discharge end.

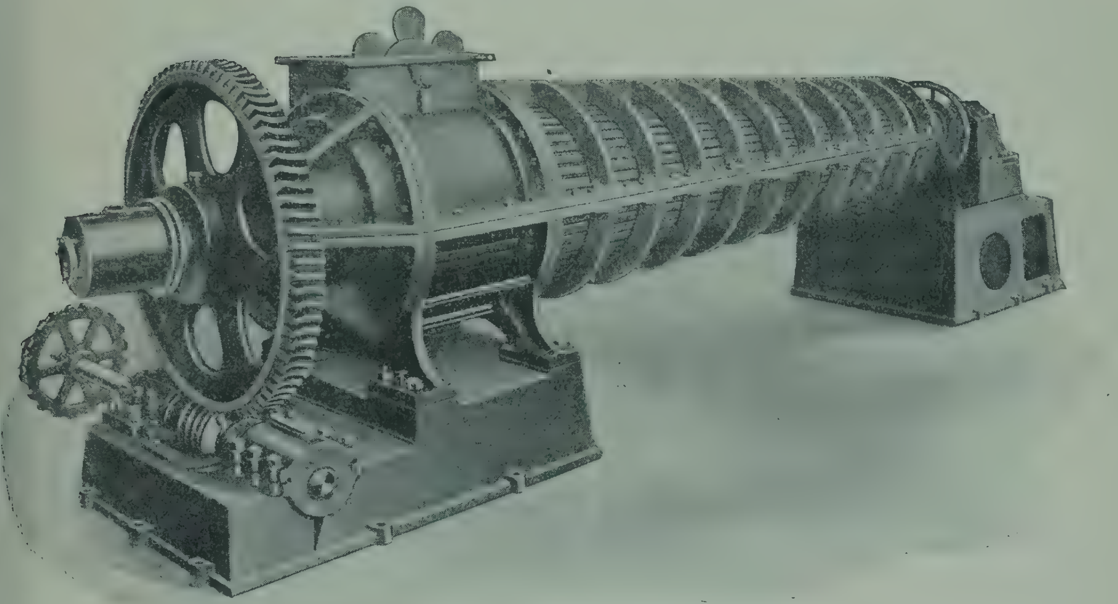
Steam may be passed into the material from the shaft during pressing: this is advantageous in pressing substances which contain much grease or oil. The water and oil which separate during pressing drain away into large settling tanks where the oil is separated. From the discharge end of the press the material is fed to the **drier**. That shown in Fig. 13 (C) is a **direct heat rotary drier**, and reduces the moisture to about 10 per cent.

The long rotating cylinder is slightly tilted from the furnace end, and is provided inside with a number of shelf-like vanes. The material and furnace gases enter at the higher end. The wet material falls to the bottom, but is elevated by the shelves to the highest point in the cylinder, and is then showered through the hot furnace gases. This operation is repeated until the dried material is discharged at the lower end of the drier.

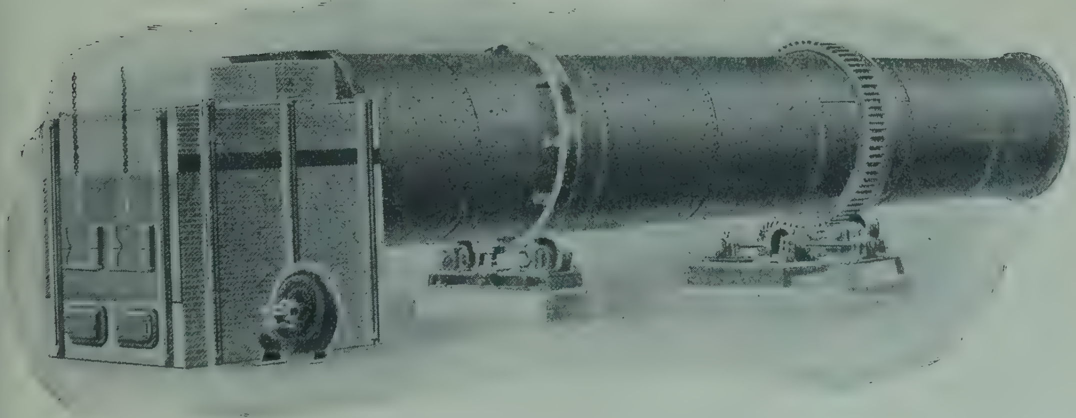
Wet Fish Scrap.—In some cases the fish scrap as it comes from the press is acidulated with sulphuric acid of 60° Bé. (60-80 lbs. per ton of wet scrap). This converts the bone phosphates into the soluble form, and also prevents the material from decomposition. Good fish scrap contains 50 per cent. water, and 7·5-7·75 per cent. ammonia.



(A) Automatic Continuous Cooker or Digester.



(B) Automatic Continuous Screw Press.



(C) Direct Heat Rotary Drier (with ring gear).

FIG. 13.

(American Process Co., New York.)

Whale Meal (or whale guano) is a variety of fish manure made from the refuse from whales.

The oil should be removed as completely as possible from fish scraps, because if present in the manure it hinders the decomposition, and is itself useless as a manure. Dry fish manure should be stored carefully on account of its great combustibility due to the residual oil. If stored in large heaps, fires may be caused by spontaneous combustion.

Analyses of Fish Guanos. (H. Richardson & Co., York.)

	Fish Meal.	Whale Meal.
Moisture	9.10	5.74
* Organic matter and water of combination	65.44	59.98
Phosphoric acid	8.82	12.79
[Equal to calcium phosphate]	[19.28]	[27.93]
Lime	10.10	16.60
Magnesia, alkalis, etc.	3.32	1.87
Insoluble siliceous matter	3.22	3.02
	100.00	100.00
* Containing nitrogen	7.21	6.63
Equal to ammonia	8.75	8.06

III. NITROGENOUS MANURES

(*a*) **Inorganic—Nitrate of Soda**, or **Sodium Nitrate,** $NaNO_3$ (Chile saltpetre) (for occurrence, preparation, etc., see Vol. I., p. 431).—This is one of the most concentrated forms of nitrogen, and a manure in which the nitrogen is in a condition very easily available by plants. The reason for this is that nitrate is very soluble in water.

The usual standard for good quality nitrate of soda is "at least 95 per cent. purity," *i.e.*, containing 15.6 per cent. nitrogen, equivalent to 19 per cent. ammonia.

The base soda (Na_2O) of the nitrate can hardly be called a fertilising ingredient, but it is beneficial because its action on clays in the soil causes decomposition, during which potash is liberated. This manure is chiefly used as a top dressing on account of its great solubility. The effect on the plant can be seen in a few hours by a change in the colour of the leaves.

Chile Saltpetre is not a complete manure, since it supplies only one essential constituent of plant food, *i.e.*, nitrogen, and for most purposes it should therefore be used in conjunction with phosphates, etc.

Ammonium Sulphate, $(NH_4)_2SO_4$ (for preparation, etc., see Vol. I., pp. 453 *et seq.*).—This is practically the only ammonium compound on the market as a fertiliser. Ammonium sulphate contains about 20-21 per cent. nitrogen, equivalent to 24-25 per cent. ammonia.

The nitrogen in the form of ammonia is not so easily assimilated by plants as it is in the nitrate form: this is because the ammonia has to be converted into nitrate in the soil by the action of nitrifying bacteria before being available for plant use (see Vol. I., pp. 427-429).

The addition of **Common Salt** to ammonium sulphate is said to increase the fertilising power (*Journ. Soc. Chem. Ind.*, 1911, p. 499).

Ammonium sulphate should not be applied to soil soon after liming, and is not very suitable (unless on grass) for wet clay soils where the want of good aeration makes the nitrifying process slow and imperfect. It is a very valuable nitrogenous manure for corn crops, potatoes, etc., while it is very suitable for making mixed manures (see p. 41). It should not be used too frequently on soils poor in lime

Calcium nitrate, lime nitrate, lime saltpetre, $Ca(NO_3)_2 \cdot 2H_2O$ (for preparation, properties, etc., see Vol. I, p. 435).—This is a comparatively new fertiliser, and is rapidly becoming a valuable nitrogenous manure, competing closely with sodium nitrate.

Nitrate of lime usually contains about 13 per cent. nitrogen, equivalent to 16 per cent. ammonia (if of 95 per cent. purity it contains 15.6 per cent. nitrogen equal to 19 per cent. ammonia), and is directly assimilable by plants without having to undergo any change in the soil. It is hygroscopic, and is best employed in the basic state [$Ca(NO_3)_2.CaO$] on account of its greater stability.

It can be rendered dry and non-deliquescent by mixing with an absorbent substance, such as sodium sulphate or calcium sulphate. A mixture of solutions of calcium nitrate and nitrite on evaporation (the nitrate nitrogen being less than 15 per cent. of the total) forms a dry, friable powder which is not deliquescent.

Calcium nitrate, like sodium nitrate, is specially suitable for top dressing on account of its hygroscopic nature, which causes it to find its way into the soil very easily. It is of special value in heavy soils and those deficient in lime.

The results of recent experiments show that nitrate of lime is one of the best of the artificial manures.

(*b*) **Organic—Calcium Cyanamide** ("lime nitrogen" or "nitrolime").—This is the calcium compound of hydrocyamic acid, $Ca=N-C\equiv N$ (for preparation, etc., see Vol. I., p. 475). It is a black compound and contains 21–22 per cent. nitrogen, 20–30 per cent. lime, and 11–12 per cent. carbon. When exposed to the air water is taken up by the lime, but there is no loss of nitrogen, as was formerly supposed. The "equivalent" hydrated lime is approximately 70 per cent.

Calcium cyanamide made by modern methods is free from the impurities present in the earlier material, such as carbides, phosphides, and sulphides. As described in Section XLIX., Vol. I., it is now usually sold as a dust-free powder, suitable for use in formulating mixed fertilisers, or in granular form, to facilitate direct application. When used properly, that is when applied some time before planting so as to undergo the necessary chemical changes before it is absorbed, nitrolime is a valuable fertiliser, since not only does it supply nitrogen, but it supplies more lime than any other fertiliser, and it is not readily leached from the soil.

The use of nitrolime as a manure depends on the reaction it undergoes with water into calcium carbonate and ammonia—

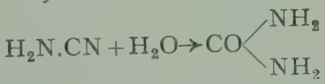
$$CaN.CN + 3H_2O \rightarrow CaCO_3 + 2NH_3.$$

Its decomposition in the soil is not so simple as shown by this equation, but probably takes place in stages.

First atmospheric carbon dioxide and water form cyanamide—

$$CaN.CN + CO_2 + H_2O \rightarrow CaCO_3 + H_2N.CN.$$

Then this is converted into urea by further action—



$$H_2N.CN + H_2O \rightarrow CO\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}$$

Urea by ammonia fermentation yields ammonium carbonate—

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3.$$

This can be assimilated either direct by plants or indirectly after being converted into nitric acid by nitrifying bacteria.

According to M. Smock (Ohio Agricultural Experiment Station Bulletin, 555), ammonification is almost coincident with hydrolysis.

The presence of the lime in calcium cyanamide has a valuable action during manuring: it prevents the soil becoming acid, thereby causing abundant growth of the nitrifying bacteria, which cannot live in acid soil.

A valuable and stable "nitrolime" fertiliser can be made by mixing equal parts of calcium nitrate and calcium cyanamide in a suitable grinding mill.

Nitrolime, as now manufactured, can be stored for a good time under ordinary conditions without damage or loss of fertilising power, and may be mixed in any proportion with other manures without evolution of heat or loss of ammonia. It is claimed that, unit for unit, nitrolime is equal in value to sodium nitrate or ammonium sulphate, but it is not suitable for top dressing, although it does not injure germination. It is a good deal dependent upon the season for its rapidity of action.

Because of its basic properties, calcium cyanamide is a valuable component of mixed fertilisers containing acid producing substances, such as ammonium sulphate, nitrate, and superphosphate. Where manufacturers have ample storage room it is good practice to formulate to a given analysis and then to put down the basic mixture to cure for a few days before bagging. Typical general purpose formulations are—

	7·14·0	3·12·6
Calcium cyanamide -	60 lbs.	60 lbs.
Ammonium sulphate -	410 ,,	100 ,,
Ammonium nitrate -	130 ,,	80 ,,
Superphosphate - -	1,400 ,,	1,200 ,,
Potassium chloride -	...	200 ,,
Dolomite or dry filler -	...	360 ,,
	2,000 lbs.	2,000 lbs.

These basic mixers, after curing, can then be used for mixing complete fertilisers without danger of caking or setting. Typical formulæ are—

Cured base 7·14·0	1,430 lbs.	1,143 lbs.	Cured base 3·12·6	1,335 lbs.
KCl	167 ,,	267 ,,		67 ,,
Dolomite	403 ,,	200 ,,		208 ,,
Cyanamide	...	390 ,,		390 ,,
	2,000 lbs.	2,000 lbs.		2,000 lbs.

Rape Cakes and **Meals** (for manufacture see **Martin's** "Industrial Chemistry: Organic" (**Oil Extraction**)).—These contain about 4·5 per cent. nitrogen, and a little potash and phosphates. **Rape cakes** and **Rape dust** are gradually decomposing fertilisers, and are specially suitable for potatoes and corn. They are prepared from rape seed which has not been completely oil-extracted. The best variety is East Indian rape cake, in which the nitrogen is as much as 6.5 per cent.

Rape Seed Meal, on the other hand, is produced by the newer chemical oil-extracting processes, and the nitrogen content is somewhat higher than in rape dust; the price is, however, lower because it takes longer time to decompose in the soil.

Castor Oil Meals are similar in character to rape meals, and are the residues from the castor oil beans after chemical extraction of the oil. For manufacture see **Martin's** "Industrial Chemistry: Organic" (**Oil Extraction**).

Similar manures are often made from damaged feeding cakes, etc.

ANALYSES OF THESE MANURES. (J. Richardson & Co., York.)

	East Indian Rape Cakes.	Oil-Extracted.	
		Rape Seed. Meal.	Castor Meal.
Moisture - - - - - - -	10.84	10.88	10.34
*Organic matter - - - -	81.14	72.78	79.42
†Phosphoric acid - - - -	2.43	1.92	1.52
Lime - - - - - - -	1.30	2.60	1.08
‡Magnesia, alkalis, etc. - - -	2.59	4.00	3.30
Insoluble siliceous matter - - -	1.70	7.82	4.28
	100.00	100.00	100.00
* Containing nitrogen - - -	5·32	5·12	4.60
Equal to ammonia - - - -	6.46	6.21	5.60
† Equal to tribasic calcium phosphate -	5·31	4.10	3·32
‡ Containing potash - - - -	1.42	1.40	1.19

Blood Meal is a very rich manure, containing on an average 11-13 per cent. nitrogen and 0.75 per cent. phosphoric acid, and rots rapidly in the soil. It is prepared by coagulating blood from slaughter-houses, etc., drying and grinding the product. The manufacture is carried on in America, and also in our own country, the product fetching a good price.

Blood meal is becoming less used as a manure, its place being taken by chemical manures. Dried blood is now mostly bought by manufacturers and converted into compound manures.

Horn and Hoof Meals.—Scraps of horn, hoof shavings, etc., are ground to form a meal; sometimes, however, they are heated or treated with superheated steam previous to grinding.

The meal must be finely ground, because horn is insoluble and decays slowly. The product is very rich in nitrogen, containing some 14 per cent. or more, and is chiefly used for vines, roses, and making mixed manures. The use as a manure is becoming less.

Wool, Shoddy, Rags, etc.—These are not suitable manures for ordinary farming, but are useful for crops such as hops and grapes. Wool, when dry, often contains 16-17 per cent. nitrogen, and as shoddy 13 per cent. The wool in shoddy is finely broken up by mechanical means.

These products are useful if obtained cheap; the value is diminished if they contain oil and dirt. Sulphuric acid is sometimes mixed with shoddy to form a manure (English Patent, 24,647, 1906). Hair and feathers form a fertiliser of similar composition to the above. The principal protein substance in all these is "Keratin."

Skin and Leather Meals.—The trimmings and waste from leather works are ground so as to form a meal. Samples of ground leather are difficult to obtain, the trade being a hidden one, and the product sold under the name of "Nitrogenous Fertiliser." The meal contains 4-6 per cent. nitrogen, and is little used as a manure on account of its slow decomposition. According to English Patent, 11,644, 1908, the residue from the dry distillation of leather is used as a manure.

Suitable products for manuring may be prepared by treating wool, leather, horn, etc., with superheated steam, sulphuric acid, or both, and a solvent like benzene for removing fat (English Patents, 12,844, 1910, and 27,266, 1911; also French Patent, 437,628, 1911, and U.S. Patent, 1,049,482, 1913).

Soot may contain up to 35 per cent. ammonium sulphate, and has been much used for manurial purposes. Soot also exerts a mechanical effect on clay lands. In buying soot for farming, care should be taken to obtain **chimney soot** rather than **shaft soot**, which only contains a little nitrogen.

Analysis of Soot (*Mark Lane Express*, 1913, Vol. CIX., p. 579):—

	Shaft Soot.	Chimney Soot.
Nitrogen - - - - - - - -	0.26	6.72
Equal to ammonium sulphate - - -	1.7	38.7
Ash - - - - - - - -	62.48	18.04
Moisture - - - - - - - -	17.0	6.59

Bacterial Manures.—Many such manures have been tried from time to time, but so far have not proved very satisfactory.

They chiefly consist of pure cultures of bacteria from the nodules that occur on the roots of leguminous plants (English Patent, 694, 1901).

These bacteria are able to assimilate nitrogen direct from the air, but only in the presence of carbon compounds (*Chemical News*, 21st September 1910).

It is still held by one class of agriculturists that soil inoculation is one of the solutions of the great problem of manuring for certain crops.

Nitragin is a culture of bacteria occurring in the nodules of legumes. The chief organism is *B. radicicola*. Pure cultures of this bacillus have not been found successful for soil inoculation. It is best to prepare the culture from several varieties of nodules, *i.e.*, peas, beans, etc.

Cultures of azotobacter and pseudo-monas have been tried with some success.

English Patent, 19,902 (1908), and U.S. Patent, 982,560 (1911), deal with the preparation of a culture of organisms that will increase the growth of non-leguminous plants.

Use of Waste Products for Making Manures.—This should be an important source of both nitrogen, phosphates, and potash, and should receive careful attention from the chemist.

Many patents exist for the utilisation of waste products for making fertilisers.

The chief ingredients of these fertilisers are wastes from breweries and distilleries, waste tanning materials, and waste cellulosic materials of all descriptions. Straw alone, when allowed to ferment, is a good fertiliser, whilst the decaying material is able to absorb urine, sewage, etc., and such mixtures are valuable artificial manures. "Tankage," often used in the U.S.A., is a mixture of scrap meat, bones, and animal intestines. This is first cooked, the fat extracted, filter pressed, dried, and ground. It contains up to 10 per cent. of nitrogen and up to 20 per cent. of tricalcium phosphate.

IV. POTASH MANURES

Potash in some form is almost indispensable to the growth of all cultivated crops; it is needed for the production of albuminoids, and helps the formation of carbohydrates. Potash occurs in all parts of the plant, and particularly in the seeds; about one-third of the ash of plants is K_2O.

The effect of potash manuring varies according to the soil; cultivated land is not usually poor in potash. Sandy, gravelly, chalky, and peaty soils, as well as reclaimed fenland and moorland, are those on which potash is most likely to have a good effect. These manures are profitable, especially for meadow grass, clover, tobacco, cotton, coffee, potatoes, legumes, corn, etc.

Production of Potash Minerals.—The following figures relating to the World production of potash salts are abstracted from "The Mineral Industry," Statistical Summary, Imperial Institute, London. They are expressed as long tons of potassium oxide and relate to the last pre-war year (1938), and the first complete post-war year (1946):—

Country and Type.	1938.	1946.
Palestine—		
Muriate - -	28,000	44,000
India—		
Nitrate - - -	3,800	1,700
France—		
Sylvinite - -	571,000	505,000
Germany—		
Kainite, carnallite -	1,420,700	...
Poland—		
Sylvite, kainite -	106,750	...
Spain—		
Carnallite, sylvinite	8,000	114,000
U.S.S.R.—		
Crude salts - -	120,000	...
U.S.A.—		
Mixed - - -	283,000	910,500
Total -	2,550,000	2,210,000

The following are the chief Potash Manures:—

Kainit (see Vol. I., p. 330).—This is a natural salt from Stassfurt, and is a cheap manure. It usually contains about 23 per cent. potassium sulphate (equal to 12.5 per cent. K_2O), 27 per cent. magnesia salts, and 4 per cent. common salt. The colour is white to reddish brown, but this is no evidence as to the quality.

Muriate of Potash (potassium chloride, KCl, see Vol. I., p. 335) is the most concentrated and soluble salt of potash, consequently it is suitable for top dressing. The potash content varies according to the purity of the salt, and is usually 50-55 per cent.

Sulphate of Potash (K_2SO_4, see Vol. I., p. 337) is not so soluble as the chloride, but nevertheless is an excellent manure. As generally sold, it is of 90-95 per cent. purity, containing about 48-52 per cent. potash.

Nitrate of Potash (KNO_3, see Vol. I., p. 433) is an excellent manure, because it contains both nitrogen, as nitrate, and potash. When pure the cost is too high to enable it to be used as a manure, but impure nitrate can be obtained at a moderate price. The purity of such nitrate is about 95 per cent., and it contains 44 per cent. potash as well as 13 per cent. nitrogen (equal to 16 per cent. ammonia).

Other potassium salts used for manuring are carnallite, kieserite, potassium phosphate, and furnace flue dusts.

V. MISCELLANEOUS MANURES

Salt (sodium chloride, NaCl, Vol. I., p. 261).—This is useful for applying to mangels, cabbages, and other crops, so-called "broad" salt or ground rock salt being used for the purpose. Soiled fish curing salt contains a certain amount of oil, and is not very effective for agricultural use. It can be obtained at a low price.

Calcium or Lime Manures are used on soils which contain little calcium.

Quicklime (see p. 78, also Vol. I., p. 341) is of great use in order to neutralise the acidity of the soil which hinders the growth of the nitrifying organisms. Lime also tends to improve the mechanical condition of the soil, increasing its porosity and general condition. Sometimes slaked lime is used, but this is heavier than quicklime, and consequently the cartage is more expensive.

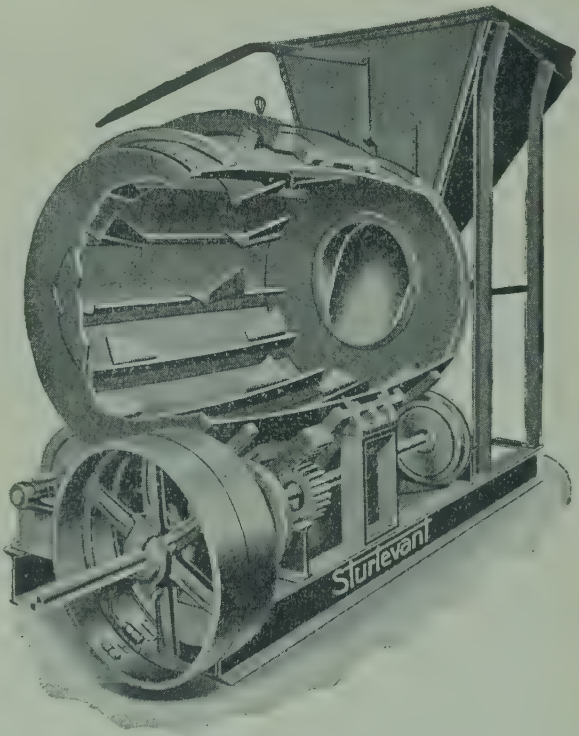


FIG. 14.—Interior View of Mixing Machine.
(*Sturtevant Engineering Co. Ltd., London.*)

Calcium Carbonate (see p. 78, also Vol. I., p. 341).—Unburnt limestone has been found to be better than quicklime on certain soils, especially on light porous soils. The cost is less than lime, but the amount of lime in limestone is only 56 per cent. Ground shells have been used as a calcareous manure.

Calcium carbide residues may be used on the soil, according to Gelach and Schulze, without harm.

Silicate Manures.—Plants cannot assimilate silica in the form of quartz. According to Witt, waterglass and potassium silicate possess great possibilities as manures, particularly for growing maize and cereals which contain much silica.

Calcium Sulphate (Gypsum) is a useful soil conditioning agent and has been used successfully for reclaiming land that has been inundated by the sea, for example, in the Fen District, in Holland and Belgium.

VI. MIXED MANURES

Manures containing more than one fertilising ingredient may be made by mixing together two or more manures of a special character in suitable proportions.

It is very important to mix the fertilising materials thoroughly in order to obtain a product of uniform composition, and consequently efficient mixing machines should be used. Fig. 14 shows the interior view of the "Sturtevant Hurso Mixer." This machine is capable of mixing to an accuracy of 0.1–0.01 per cent., with an output up to 400 tons of material per day. There are many other types of mixers on the market. The formulation of complete mixed fertilisers is also discussed on p. 38.

Potassic Superphosphate is made by combining calcium superphosphate and potash salts.

Saltpetre Superphosphate is likewise made by mixing nitre and superphosphate. It is not liked because free nitric acid is developed, and this corrodes the sacks and even causes them to catch fire.

Artificial Guanos are prepared by mixing nitrogenous and phosphatic manures such as calcium superphosphate and ammonium sulphate in varying proportions. The mixture changes partly into ammonium phosphate and calcium sulphate, and is sold under the name of "nitro-phosphate" or sometimes wrongly called "ammonium superphosphate."

Certain manures should not be mixed. For instance, nitrolime should not be mixed with guanos, etc., and if mixed with superphosphate causes part of the soluble phosphate to be reverted, although there is no loss of nitrogen.

VII. GUANOS

(*a*) **Raw Peruvian Guano** is obtained from the huge deposits of excreta, up to 100 ft. thick, from extinct as well as present-day birds at Ballestas and other islands, and along the Pacific coast of Peru.

The birds are chiefly pelicans and cormorants and deposit 20,000–30,000 tons per year.

These deposits vary in composition; some are rich in nitrogen, and others in phosphates. In general, when one constituent is present in a large amount, the proportion of the others is comparatively low. The ammonia in guano varies from about 2-12 or 14 per cent., calcium phosphate from 20-60, and potash 1.5-4 per cent.

Sometimes guanos are blended or mixed with chemical manures, such as ammonium salts, in order to obtain definite proportions of phosphates and nitrogen. The product is sold as "**equalised guano.**" The Peruvian guanos are gradually becoming exhausted, but the Peruvian Government have limited the removal of the guano so as not to disturb the birds, and hope in this way to extend the supply.

Recent figures for the output of Peruvian guano are not available. The principle producing areas now appear to be the Seychelles group of islands in the Indian Ocean. These produced approximately 20.000 tons of guano in both 1938 and 1946.

(*b*) **Ichaboe Guano** is obtained from the Ichaboe group of islands off the south-west coast of Africa. Deposits of guano are formed by recent birds, and dry naturally. The deposit is collected after the birds have migrated.

Ichaboe guano is a rich nitrogenous and phosphatic manure, and compares well with the Peruvian guanos, the price being decidedly less.

(*c*) **Riddled Guano.**—Ordinary raw guano is in a lumpy condition, and contains some stones. Riddled guano is made by removing the stones and reducing the lumps to a powder.

Sometimes guanos are treated with acid in order to obtain a product which is more soluble and of use for top dressing. This is sold as "**dissolved guano**."

Natural guanos have a decided advantage over mixtures of ammonium salts, phosphates, etc., because the nitrogen and phosphates are closely associated.

Products obtained from Sewage Sludge, Town Refuse, etc.—Many attempts have been made to utilise human fæcal substances for manuring and dried sewage material is now supplied by many local authorities. Sludge produced by certain processes for treating sewage (see Vol. I., p. 191) is used in places as a manure, and gives very excellent results.

A manure sold as "**native guano**" is prepared as follows by pressing sludge which is pumped under a pressure of some 70 lbs. per square foot into **filter presses** (see **Martin's** "Industrial Chemistry: Organic," pp. 33, 34).

The liquid drips into a channel underneath the press. Filtration is carried on until the filter press chambers are completely full, and no more liquid drips from them. The press is now opened, and the solid cakes removed.

With a press of plates 30 in. square, and 1½ in. deep, seventy cakes weigh a ton.

The cakes are next air-dried and ground. The product is a very excellent fertiliser, and is sold at about £3. 10s. per ton.

The **native guano** (as supplied by the Native Guano Co.) was found on analysis to contain the following: Nitrogen 4.59 per cent. (equivalent to 5.57 ammonia), phosphoric oxide 2.15 per cent., and a little potash.

A patent drier for drying sewage sludge, wet grain, etc., by means of superheated steam is supplied by Messrs Blair, Campbell, & M'Lean, of Glasgow.

There are many other methods for preparing manures from sewage sludge. Some of the chief are: treatment with sulphuric acid; by distilling sludge; by treating with a precipitant, such as lime or chalk; by bacterial treatment.

Plants have been designed for utilising town refuse, street sweepings, etc. The chief processes consist in treatment of the refuse with sulphuric or nitric acids, or with heat or superheated steam.

Manures made from town refuse and sewage are usually poor in fertilising constituents, and must therefore be used in large quantities. Under these circumstances the cost of carriage becomes a serious element in deciding when and where they can be economically used.

Seaweed contains 1-3 per cent. nitrogen, 3 per cent. potash, and 0.5 per cent. phosphoric acid. According to English Patent, 27,257, 1912, seaweed is dried and powdered, gelatinous matter being added.

Farmyard Manure.—This has been used since very early times. It consists of the dung and urine of animals together with litter, and contains complete nourishment for the plant as well as humus-forming substance. Such manure contains on an average 0.4 nitrogen, 0.5 potash, 0.15 phosphoric oxide, and 0.45 lime per cent.

The most important constituent is the nitrogen. This is greater in manure from sheep and horses than from cattle and pigs.

Farmyard manure loses part of its nitrogen (as ammonia, and also as free nitrogen) while it is lying in heaps. Efforts have been made to prevent the loss by adding sulphuric acid or gypsum in order to fix the ammonia, but so far have not proved very satisfactory.

VIII. THE FERTILISERS AND FEEDING STUFFS ACT, 1906

[6 Edw. VII., chap. 27.]

Some of the chief parts of this Act dealing with fertilisers are:—

1. (1) "Every person who sells for use as a fertiliser of the soil, any article which has been subjected to any artificial process in the United Kingdom, or which has been imported from abroad, shall give to the purchaser an invoice stating the name of the article, and what are the respective percentages (if any) of nitrogen, soluble phosphates, insoluble phosphates, and potash contained in the article, and the invoice shall have effect as a warranty by the seller that the actual percentages do not differ from those stated in the invoice beyond the prescribed limits of error."

1. (5) "Any statement by the seller of the percentages of the chemical and other ingredients contained in any article sold for use as a fertiliser of the soil . . . made after the commencement of this Act in an invoice of such article, or in any circular or advertisement descriptive of such article, shall have effect as a warranty by the seller."

1. (6) "Where an article sold for use as a fertiliser of the soil . . . consists of two or more ingredients which have been mixed at the request of the purchaser, it shall be a sufficient compliance with the provisions of this section with respect to percentages if the invoice contains a statement of percentages with respect to the several ingredients before mixture, and a statement that they have been mixed at the request of the purchaser."

Limits of Error (Fertilisers and Feeding Stuffs Regulations, 1906).—The percentage should be within the limits of error. Thus, if the phosphates are 20 per cent., then the article should contain 19-21 per cent. of phosphate. It is doubtful whether these limits are sufficiently elastic to cover the inevitable variation of samples and of the tests used by different chemists.

	DESCRIPTION OF FERTILISER.	LIMITS OF ERROR			
		Soluble Phosphates.	Insoluble Phosphates.	Nitrogen.	Potash.
1	Superphosphates	1	...	...	...
2	Dissolved raw bones :—				
	(*A*) When total percentage of phosphate is 32 or more per cent.—				
	(*a*) If excess of actual percentage of insoluble phosphate over that stated in the invoice is 3 or more per cent.	4	...	·3	...
	(*b*) If excess is between 3 and 2 per cent.	3	...	·3	...
	(*c*) If excess is between 2 and 1 per cent.	2	...	·3	...
	(*B*) In all other cases	1	1	·3	...
3	Bone compounds	1	1	·3	...
4	Compound manures (other than bone compounds, but including dissolved or equalised guano)—				
	(*a*) If respective percentage of nitrogen and of phosphate stated do not exceed 4 per cent.	1	1	·3	·3
	(*b*) If such exceed 4 per cent.	1	1	·5	·5
5	Sulphate of ammonia	...	...	·5	...
6	Nitrate of soda	...	...	·5	...
7	Ground hoofs and horns	...	...	·5	...
8	Dried blood	...	...	·5	...
9	Fish guano and meat meal	...	2	·5	...
10	All cakes and meals (other than bone and meat meals)	...	...	·5	...
11	Ground bones and bone meal	...	2	·5	...
12	Basic slag and basic superphosphate	2 (Soluble in 2 per cent. citric acid.)	2	...	...
13	Shoddy, wool and hair waste	...	...	1	...
14	Kainit and other potash salts—				
	(*a*) Where percentage of K_2O is not over 15 per cent.	...	...	...	1
	(*b*) Where percentage of K_2O exceeds 15 per cent.	...	...	...	2
15	Nitrate of potash	...	...	·5	2
16	Peruvian and other natural imported guanos—				
	(*a*) Where insoluble phosphates do not exceed 30 per cent.	...	3	...	·5
	(*b*) Where such exceeds 30 per cent.	...	5	...	·5
	(*c*) Where the percentage of nitrogen stated does not exceed 3 per cent.	...	...	·5	·5
	(*d*) Where such percentage is between 3 and 5 per cent.	...	...	·75	·5
	(*e*) Where such percentage is over 5 per cent.	...	...	1	·5

Analysis of Manures.—This is carried out according to the Regulations of the Board of Agriculture, 1908 (see *Analyst*, 1909, p. 462).

I. Determination of Moisture (loss on drying).

A weighed quantity of the sample shall be dried at 100° C.

II. Determination of Nitrogen.

The presence or absence of nitrates must first be ascertained.

(A) **Nitrogen in the Absence of Nitrates.**—(*a*) A weighed portion of the sample shall be transferred to a Kjeldahl flask; 10 g. of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask heated until a clear, colourless, or light straw coloured liquid is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a small globule of mercury to the liquid in the flask.

(*b*) The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and where mercury is used, with the addition also of sodium or potassium sulphide solution.

(B) **Nitrogen when Nitrates are Present.**—(*a*) A weighed portion of the sample shall be transferred to a Kjeldahl flask; 30 c.c. of concentrated sulphuric acid added (containing 1 g. of salicylic acid), and the flask shaken so as to mix the contents without delay. The shaking shall be continued at intervals for ten minutes, the flask being kept cool, and then 5 g. of sodium thiosulphate and 10 g. of potassium sulphate added. The flask shall now be heated until the contents are colourless or nearly so. Copper sulphate or mercury may be used as above (II. (A) (*a*)).

(*b*) The quantity of ammonia shall be determined in exactly the same way as above (II. (A) (*b*)).

(C) **Nitrogen in the Form of Ammonium Salts.**—A weighed portion shall be taken and transferred to a flask, and the ammonia determined in the way described in II. (A) (*b*).

(D) **Nitrogen in Nitrates in the Absence of Ammonium Salts, and of Organic Nitrogen.**—1 g. of the sample shall be placed in a ½ litre Erlenmeyer flask with 50 c.c. of water. 10 g. of reduced iron and 20 c.c. of sulphuric acid of 1.35 sp. gr. shall be added. The flask shall now be closed with a rubber stopper provided with a thistle funnel, the head of which shall be filled with glass beads. The liquid shall be boiled for five minutes, and the flask removed from the flame; any liquid which may have accumulated on the beads shall be rinsed back into the flask with water. The solution shall now be boiled for three minutes more. and the beads again washed with water. The ammonia shall then be estimated as above (II. (A) (*b*)).

In the cases in which the proportion of nitrates is small, a larger quantity of the sample shall be taken.

(E) **Control Experiments in the Determination of Nitrogen.**—The materials used in any of the methods described under this paragraph (II.) shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions, with the same quantities of reagents which have been employed in the actual analysis, in the case of (A), 1 g. of pure sugar being used in the place of the weighed portion of the sample. The quantity of standard acid used in the control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.

III. Determination of Phosphates :—

(A) **Phosphates Soluble in Water.**—In the case of superphosphates, dissolved bones, and similar substances, 20 g. of the sample shall be continuously agitated for thirty minutes in a litre flask with 800 c.c. of water. The flask shall then be filled up to the mark and again shaken, and the contents shall be filtered. 50 c.c. of the filtrate shall be boiled with 20 c.c. of concentrated nitric acid, and the phosphoric acid determined by the molybdate method prescribed below in paragraph III. (D). In the case in which the proportions of phosphates soluble in water is small, a larger quantity of the filtrate prepared as above shall be taken.

(B) **Phosphates Soluble in the Prescribed Citric Acid Solution.**—5 g. of the sample shall be transferred to a stoppered bottle of about a litre capacity. 10 g. of pure crystallised citric acid shall be dissolved in water, the volume shall be made up to 500 c.c., and the solution shall be added to the weighed sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 c.c. of methylated spirit or alcohol before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 c.c. instead of 500 c.c. The bottle shall at once be fitted to a shaking apparatus, and shall be cautiously agitated during thirty minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper. 50 c.c. of the filtrate shall then be taken, and the phosphoric acid shall be determined by the molybdate method prescribed below in paragraph III. (D).

(C) **Total Phosphoric Acid.**—A weighed portion of the sample, in which portion, if necessary, the organic matter has been destroyed by ignition, and the silica removed by appropriate means, shall be dissolved in nitric acid and boiled, the solution being made up to a definite bulk.

The phosphoric acid shall be determined in an aliquot part of the solution by the molybdate method in paragraph III. (D).

(D) **Molybdate Method.**—To the solution, which should preferably contain 0.1-0.2 g. of phosphoric oxide, obtained as above described in paragraphs III. (A), (B), or (C), 100-150 c.c. of molybdic acid solution, or an excess of such a solution—*i.e.*, more than sufficient to precipitate all the phosphoric oxide present in the solution—shall be added, and the vessel containing the solution be placed in a water bath maintained at 70° C. for fifteen minutes, or until the solution has reached 70° C. It shall then be taken out of the bath and allowed to cool, and the solution filtered, the phospho-molybdate precipitate being washed several times by decantation, and finally on the paper with 1 per cent. nitric acid solution. The filtrate and the washings shall be mixed with more molybdic acid solution, and allowed to stand in a warm place in order to ascertain that the whole of the phosphoric oxide has been precipitated.

The phospho-molybdate precipitate shall be dissolved in cold 2 per cent. ammonia solution, prepared as described below, and about 100 c.c. of the ammonia solution shall be used for the solution and washings. 15-20 c.c. of magnesia mixture, prepared as described below, or an excess of such mixture—*i.e.*, more than sufficient to precipitate all the phosphoric oxide present—shall be added drop by drop, with constant stirring. After standing at least two hours with occasional stirring, the precipitate shall be filtered off, washed with 2 per cent. ammonia solution, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings shall be tested by the addition of more magnesia mixture.

(E) **Preparation of Molybdic Acid Solution.**—125 g. of molybdic acid and 100 c.c. of water shall be placed in a litre flask, and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 c.c. of 8 per cent. ammonia solution, prepared as described below. 400 g. of ammonium nitrate shall be added, the solution made up to the mark with water, and the whole added to 1 litre of nitric acid (sp. gr. 1.19), the solution maintained at about 25° C. for twenty-four hours, and then filtered.

(F) **Preparation of Magnesia Mixture.**—110 g. of crystallised magnesium chloride and 140 g. of ammonium chloride shall be dissolved in 1,300 c.c. of water. This solution shall be mixed with 700 c.c. of 8 per cent. ammonia solution, and the whole shall be allowed to stand for not less than three days, and shall then be filtered.

(G) **Preparation of Ammonia Solutions** :—

(i.) 8 per cent. ammonia solution.—One volume of ammonia solution of sp. gr. 0.880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition of strong ammonia or water as required until it has the sp. gr. of 0.967.

(ii.) 2 per cent. ammonia solution.—One volume of the 8 per cent. ammonia shall be mixed with three volumes of water.

IV. Determination of Potash :—

(A) **Muriate of Potash Free from Sulphates.**—A weighed portion of the sample (about 5 g. in the case of a concentrated muriate of potash, or 10 g. in the case of a low-grade muriate) shall be dissolved in water, the solution filtered (if necessary) and made up to 500 c.c. To 50 c.c. of the solution, placed in a porcelain basin, a few drops of hydrochloric acid shall be added, and also 10-20 c.c. (according to whether the portion weighed was 5 or 10 g.) of a solution of platinum chloride containing 10 g. of platinum per 100 c.c. After evaporation to a syrupy consistency on a water bath, the contents of the basin shall be allowed to cool, and shall then be treated with alcohol of sp. gr. 0.864, being washed by decantation until the alcohol is colourless. The washings shall then be passed through a weighed or counterpoised filter paper, on which the precipitate shall be finally collected and washed with alcohol as above, dried at 100° C. and weighed. The precipitate is to be regarded as K_2PtCl_6.

(B) **Salts of Potash containing Sulphates.**—A weighed portion of the sample (about 5 g. in the case of a concentrated sulphate of potash, or 10 g. in the case of kainit or other low-grade salts) shall be boiled with 20 c.c. of hydrochloric acid and 300 c.c. of water in a ½ litre flask. Barium chloride solution shall then be cautiously added, drop by drop, to the boiling solution, until the sulphuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulphuric acid. The liquid (without filtration) shall be cooled and made up to 500 c.c. A portion shall then be filtered, and 50 c.c. of the filtrate shall be treated as in paragraph IV. (A), 10 or 20 c.c. of platinum chloride, as the case may be, being used.

(C) **Potash in Guanos and Mixed Fertilisers.**—10 g. of the sample shall be gently ignited in order to char the organic matter, if present, and shall be heated for ten minutes with 10 c.c. of concentrated hydrochloric acid, and finally boiled with 300 c.c. of water. The liquid shall then be filtered into a ½ litre flask, raised to boiling point, and a slight excess of barium hydrate added. The contents of the flask shall be cooled and made up to 500 c.c. and filtered. Of the filtrate 250 c.c. shall be treated with ammonia solution and excess of ammonium carbonate; and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 c.c., and filtered. Of the filtrate, 100 c.c. are to be evaporated in a platinum dish, and the residue heated, first in an air bath, and then very gently over a low flame, till all ammonium salts are expelled, the temperature being kept below that of low redness. The residue shall be treated with hot water, filtered if necessary, and the potash determined in the filtrate as in paragraph IV. (A).

Forms of Certificate.—These should contain the following words: "The analysis was made in accordance with the Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations, 1908."

The Fertilisers and Feeding Stuffs Act, 1926

This Act was introduced to answer many complaints regarding the working of the 1906 Act. The scope of the Act and its implications was the subject of a recent Streatfeild Memorial Lecture by G. Taylor.(1) The scope of the Act was defined by its accompanying Schedules, which enumerated the articles to which the various provisions of the Act related, the necessity to disclose worthless ingredients of a feeding stuff, and the fertilisers and feeding stuffs that are Scheduled articles. For practical purposes the Act came into operation in 1928, with the issue of new Regulations for sampling and analysis. These were replaced by the Fertilisers and Feeding Stuffs Regulations, 1932, which have remained unaltered since, except for an Amending Order in 1942. This made slight alterations in the limits of variation in the First and Fourth Schedules. The 1932 Regulations prescribe the limits of variation, the manner in which the samples are to be taken, and other matters regarding procedure. Apart from the permissible limits of error, and the use of perchloric acid for the determination of potash, the methods of analysis are the same as those in the Regulations of 1908, relating to the 1906 Act. Taylor pointed out that although the methods of analysis in the Regulations provide a guarantee of the amount of the chemicals in a given fertiliser, they provide no information regarding the immediate "availability" of the fertilising elements present. In the U.S.A., it is generally accepted that the amount of phosphate soluble in neutral ammonium citrate solution is a measure of phosphate availability. This appears to be true, except in the case of basic slag, where solubility in dilute citric acid solution is the preferred method. Taylor advocated the immediate amendment of the Regulations to include a method for the determination of the citrate solubility of phosphates.

Statistics

Production and Import of Fertilisers, British Isles[1]

	1938.	1946.
Production, tons:		
Total ammonia products, basis 25 per cent. ammonia	...	1,430,000
Actual ammonium sulphate	...	796,700
Superphosphate - - -	551,500	1,092,000
Basic slag - - - -	465,600	589,000
Imports in tons (U.K. only):		
Potassium nitrate - -	2,460	300
Sodium nitrate - - -	46,210	45,085
Calcium nitrate - - -	5,120	...
Cyanamide- - - -	4,910	690
Ammonium chloride - -	1,530	...
Ammonium nitrate - -	1,570	...
Ammonium phosphate -	...	18,270
Anhydrous ammonia - -	43	...
Phosphate rock - - -	410,400	864,035
Superphosphates - -	14,385	204,200
Basic slag - - - -	670	10,150
Potash salts, fertilisers -	62,150	...
Potassium chloride - -	89,043	223,480
Potassium sulphate - -	43,730	2,960

---

[1] Abstracted from "The Mineral Industry," Imperial Institute. Figures rounded off by Editor.

Availability of Nitrogenous Fertilisers.—The Advisory Committee to the Act, in a Report dated 1925, referred to the possibility of distinguishing between water soluble and water insoluble nitrogen. Their conclusion was that such a statement of solubility was inadvisable since it would not necessarily indicate "availability." It is generally assumed now that certain water soluble nitrogenous compounds, such as ammonium salts, sodium, and potassium salts, are immediately available in the soil as fertilisers, but that water insoluble organic nitrogen compounds, such as waste wool, leather, casein, and plastics, only become slowly available. The nitrogen in dried blood, hoof or horn meal, fish and meat meal, become available rapidly, and calcium cyanide more slowly. Until some more certain test of nitrogen availability is developed, such as a biological method, the Act cannot be modified in this respect.

World Production and Consumption of Fixed Nitrogen.—According to the 29th Annual Report of the British Sulphate of Ammonia Federation Ltd., for the year ending 30th June 1949, world production of fixed nitrogen for all purposes during the year was 4,152.1 thousand metric tons. Total world consumption was 4,084.4 thousand metric tons, of which 85 per cent. was consumed as fertiliser.

REFERENCES

(1) G. Taylor, 30th Streatfeild Memorial Lecture, R.I.C., London, 1948.
(2) *The American Fertiliser*, **88**, 13; **89**, 1, 2 and 3 (1938).
(3) D. P. Hopkins, *Manuf. Chem.*, **18**, 205 (1947).
(4) S. Nordengren, Fertiliser Society Pub. (1947).
(5) W. B. Andrews, *Agric. Chem.*, **3**, 2, 25 (1948).
(6) K. G. Clark, J. Y. Yee, and K. S. Love, *Ind. Eng. Chem.*, **40**, 1,178 (1948).
(7) Quanquin, *Ind. Chim.*, **9**, 34, 165 (1947).
(8) D. Cairns, *Fert. J.*, **34**, 671 (1948).
(9) P. C. Marth *et al.*, *Agric. Chem.*, **10**, 42 (1948).

SECTION LV

THE INDUSTRY OF ALUMINIUM COMPOUNDS

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

LITERATURE

D. B. Hobbs.—"Aluminium, its History, Metallurgy and Uses." Milwaukee, 1938.
J. Billater.—"Technische Elektrochemie." Halle-Saale, 1932.
R. J. Anderson.—"Secondary Aluminium." London, 1933.
Thorpe's "Dictionary of Applied Science," Vol. I. London, 1945.
A. van Zeerlander.—"Technology of Aluminium and its light alloys." *Trans. A. J. Field.* Amsterdam, 1936.
See also references on page 58.

Within the last few years the industry of aluminium compounds has undergone great changes and developments. First of all, bauxite at the present time has almost entirely displaced the other raw materials used for the manufacture of aluminium compounds. Secondly, the manufacture of aluminium oxide, Al_2O_3, on the large scale for the manufacture of metallic aluminium, is now by far the most important part of the industry, and the alumina thus prepared from the hydrate must be very pure. The third great change is the gradual replacement of alum in the dyeing and other industries by aluminium sulphate—now made possible by the manufacture of the latter in a high degree of purity by means of pure aluminium hydroxide. Where the aluminium sulphate is not required of a high degree of purity (as in paper manufacture) the old methods are still used.

Manufacture of Aluminium Hydroxide, $Al(OH)_3$, and **Alumina**, Al_2O_3.—**Bauxite** is by far the most important source of aluminium compounds, being richer than any other mineral in alumina; it occurs in very large quantities in Southern France, Dalmatia, South America, Ireland, and other districts as well.

Bauxite consists principally of hydrated alumina, $Al_2O_3.2H_2O$, mixed with silica and iron hydroxide. It contains as a rule 41-70 per cent. Al_2O_3, 1-20 per cent. Fe_2O_3, 2-20 per cent. SiO_2 and TiO_2, 10-20 per cent. combined water. The following gives some typical analyses of bauxite :—

	1.	2	3.	4.	5.
Al_2O_3 - - - - -	60.98	65.02	70.38	68.50	41.08
Fe_2O_3 - - - - -	2.82	2.14	5.12	3.44	3.2
SiO_2 - - - - -	17.47	15.08	9.00	10.40	33.2
TiO_2 - - - - -	3.50	3.56			
H_2O (combined) - -	14.61	14.06	15.50	17.66	22.5

1-4 are specimens of French bauxite. 5 is a sample of Irish bauxite.

Two main processes for working the bauxite are in use, viz.—(1) **The Dry Process**; (2) **The Wet Process.**

1. **The Dry Process** of working the bauxite is as follows :—The bauxite is ground to a fine powder, mixed with calcined soda ash, Na_2CO_3, and heated in a reverberatory furnace to bright redness, carefully avoiding actual fusion.

The amount of Na_2CO_3 added varies with the kind of bauxite employed, samples rich in silica having added to them somewhat more sodium carbonate than those poorer in this constituent
From 1.2-1.8 molecules of Na_2CO_3 are added per molecule of Al_2O_3, so that not only some

normal aluminate, $Al(ONa)_3$, is produced, but also much mono-aluminate, $AlO.ONa$. The addition of more soda than this favours the fusing of the mass, and the CO_2, not being completely expelled, causes decomposition of the soluble aluminate in the subsequent lixiviation processes.

Jurisch gives the following working example: 285 kilos of a bauxite containing 60 per cent. Al_2O_3, 20 per cent. Fe_2O_3, and 17 per cent. H_2O were mixed with 250 kilos Na_2CO_3 (95 per cent.) and heated four hours, when a greenish mass weighing 362 kilos was obtained, which contained 50 per cent. of its Al_2O_3 in a soluble form.

There is thus obtained a dirty green mass of sodium aluminate, easily crumbling to a powder. This is now rapidly extracted with water, by first grinding up, then placing in a wooden vat provided with a stirring gear, and hot weak liquors from previous extractions are first poured on, finishing up with pure water, to which a little KOH or NaOH has been added. During the process heating is carried out by steam.

The soluble sodium aluminates dissolve in water, while there remains behind in insoluble form all the iron (so that for this process even iron-rich bauxites can be used), much silica, and some alumina.[1]

The process of lixiviation must be completed as rapidly as possible (five to ten minutes), for the alkaline superficial layers of the liquid are decomposed by atmospheric CO_2, depositing $Al(OH)_3$ in a crystalline form as hydrargyllit. The separation of $Al(OH)_3$ at this stage means a loss of alumina, as this would go to the insoluble residues which are filtered off. Towards the end of the extraction some NaOH or KOH is added to clear the liquid.

The liquor thus obtained should be clear, and contain at least 170 g. Al_2O_3 and 182-100 g. Na_2O in the litre. From weaker solutions $Al(OH)_3$ spontaneously separates out in a slimy condition, and causes trouble in filtering. It will be noticed that this ratio corresponds roughly to 1 mol. Al_2O_3-1.8 mols. Na_2O, whereas $Al(ONa)_3$ requires theoretically $1Al_2O_3 : 3Na_2O$. The reason is, however, that much mono-aluminate, $Al(OH)_2ONa$, and dialuminate, $Al(OH)(ONa)_2$, is present in the solution in addition to $Al(ONa)_3$. This smaller percentage of Na_2O effects economy, in that less CO_2 is required in the final precipitation of the $Al(OH)_3$.

The hot solution of sodium aluminate is rapidly sent through a filter press to free from any insoluble residue, and is then run clear into cylinders some 9 or 10 ft. high and 3-4 ft. in diameter. By means of live steam the temperature is kept at 50°-60° C., while CO_2 (obtained from coke fires or from lime kilns) is pumped through the liquid, and precipitates the alumina in a granular and easily filtrable condition.

The liquor should have a density of 35° Bé. The reaction is—

$$2Al(ONa)_3 + 3CO_2 = 2Al(OH)_3 + Na_2CO_3.$$

However, some free NaOH is present in the solution, no doubt arising from the decomposition of the sodium ferrite, $NaFeO_2$, by water, thus—

$$2NaFeO_2 + H_2O = Fe_2O_3 + 2NaOH.$$

The iron present is thus rendered insoluble. No doubt, also, a simple hydrolysing action of the water takes place thus—

$$Al(ONa)_3 + 3H_2O = Al(OH)_3 + 3NaOH.$$
$$Al(OH)_2(ONa) + H_2O = Al(OH)_3 + NaOH.$$

Another method of precipitating the $Al(OH)_3$ is that described by Bayer's patent (D.R.P., 43,977; *Chem. Zeitung*, 1888, 1893), which consists in stirring into the liquid crystalline $Al(OH)_3$. This causes all, or nearly all, the alumina in solution to separate out in a crystalline and very pure form.

The precipitated alumina is filtered off, pressed, and washed: it then contains 40 per cent. Al_2O_3, 58 per cent. H_2O, 2 per cent. Na_2CO_3, and only traces of iron. By careful washing it can be further purified.

The mother liquors from the precipitated alumina, containing sodium carbonate and some caustic soda, are evaporated down and the alkali used again.

2. **The Wet Process.**—A somewhat cheaper method of procedure is the "**wet process**," introduced by Bayer. The finely powdered bauxite is heated with conc. NaOH solution (1 mol. Al_2O_3 : 1.3 mols. NaOH) under pressure in

---

[1] The residues, after drying at 100° C., often contain 55-56 per cent. Fe_2O_3, 9-10 per cent. Al_2O_3, 7-8 per cent. SiO_2, 5-6 per cent. Na_2O, 3-4 per cent. CO_2, and 18-20 per cent. H_2O. They are often sold to gas works for purifying gas (Lux's mass). The iron, in the process of calcination, has been converted into sodium *ferrite*, $NaFeO_2$. This, when treated with water, yields insoluble Fe_2O_3 and NaOH.

kiers by steam at 70–80 lbs. pressure. The mono-aluminate, AlO.ONa, is produced and goes into solution. The solution, separated from the undissolved residue by filtering in a filter press, is now stirred continually with the addition of pure alumina from a previous batch. $Al(OH)_3$ separates—$AlO.ONa + H_2O = AlO.OH + NaOH$. The alumina is filtered off and washed. The liquors, containing all the NaOH, are concentrated and used again.

In addition to this precipitated alumina a certain amount of "colloidal alumina" is used in the textile and dye industries, being prepared by decomposing aluminium sulphate with excess of sodium carbonate solution, the precipitate being thoroughly washed.

Manufacture of Alumina and Aluminium Hydroxide from Cryolite

Cryolite, $AlF_3.3NaF$, containing more than half its weight of fluorine, occurs in a great deposit in Greenland, embedded in granite rocks. The deposit extends under the sea bed, and is now mined to the extent of some 10,000 tons a year. The bulk goes to the United States, where a large factory works it up into soda, sodium aluminate, and fluorine compounds. A similar factory also exists in Belgium.

The cryolite is finely ground, intimately mixed with limestone or chalk, $CaCO_3$, and heated in a reverberatory furnace, when sodium aluminate and calcium fluoride are produced thus—

$$3CaCO_3 + AlF_3.3NaF = 3CaF_2 + Al(ONa)_3 + 3CO_2.$$

The mass is now extracted with water, whereby the CaF_2 is left behind in an insoluble form, the sodium aluminate, $Al(ONa)_3$, going into solution.

The solution of sodium aluminate is decomposed by means of CO_2 as explained under **Bauxite**—

$$2Al(ONa)_3 + 3CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3.$$

The Na_2CO_3 solution is evaporated and sold for soda, while the CaF_2 also finds some sale.

However, cryolite is, in general, too dear a mineral to make the manufacture of Al_2O_3 by this method a very profitable matter, and most of the factories in Europe which formerly worked this process have now given it up.

The principal uses of cryolite are (1) the manufacture of opaque milk glass; (2) for manufacture of enamels; (3) as a flux in the manufacture of metallic aluminium.

Manufacture of alumina from aluminium nitride by the **Serpek process** is fully discussed in this work, Vol. I., under **Ammonia from Nitrides.**

Properties and Use of Aluminium Hydroxide, $Al(OH)_3$, and **Alumina,** Al_2O_3.—When moist, $Al(OH)_3$ is a gelatinous substance which gradually dries at ordinary temperatures to a white powder, and when ignited is converted into alumina, Al_2O_3. The substance is insoluble in water, but dissolves in dilute NaOH, KOH, and acids. However, prolonged boiling of the hydrate in water makes it insoluble both in acids and alkalis.

Aluminium hydroxide finds considerable use as a mordant in the dyeing and calico printing trades. When precipitated from solutions containing dyes, it either combines or occludes the dyes, and fixes them firmly in the cloth.

Precipitated aluminium hydrate, $Al(OH)_3$, contains no iron, and only traces of SiO_2 and Na. From this a very pure iron-free aluminium sulphate is produced by simply dissolving it in sulphuric acid—$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$.

However, the bulk of the aluminium hydroxide thus produced is ignited, whereby it is converted into **anhydrous alumina,** Al_2O_3 ($2Al(OH) = Al_2O_3 + 3H_2O$), which contains, on the average, 98–99 per cent. Al_2O_3, 0.2 per cent. Na_2O, and less than 0.2 per cent. SiO_2. Alumina is used on the large scale for the manufacture of metallic aluminium.

The process is one of electrolytic reduction based upon the work of Hall (1886) and Herault (1886), who found, independently, that a mixture of cryolite containing from 10–15 per cent. of Al_2O_3 melts at about 1,000° C. and that the alumina in solution can then be electrolysed by the passage of an electric current. In modern practice electric arc furnaces are used, carbon lined, using Soderberg electrodes. The Soderberg electrodes consist of a paste of tar and petroleum coke, contained in a thin aluminium sheath, which is fed into the molten bath as the reaction proceeds. The carbon is oxidised to CO_2. The process requires about 25,000 kW of electrical

TECHNOLOGICAL RESEARCH

energy per ton of aluminium and about 15 cwts. of carbon are also used during the process. The Al_2O_3 used is first purified, usually by the Bayer process.

Alundum is bauxite fused in the electric furnace and is the trade name used by the Norton Co., U.S.A. Crude bauxite is first calcined in rotary kilns and the calcined product is then fused in conical pots with central electrodes that can be raised as the fused bauxite fills the pots. The pots are water cooled and a thick layer of Al_2O_3 is allowed to accumulate on the inner shell. The fused mass is cooled, ground, and de-dusted. The dust is added to a further charge for remelting. The ground product is graded and used for the manufacture of grinding wheels. It is also used for the manufacture of laboratory apparatus, crucibles, muffles, filters, formers, tubes and for acid tower packings. It is also used as a refractory, because of its high melting point and good thermal conductivity.

Properties:

Melting point	2,050° C.
Thermal conductivity	.00833 C.G.S. units
Specific gravity	3.9–4.0
Hardness (Moh scale)	9–10
Sp. heat	0.18–.20 at 100° C.

Fused alumina finds some application as a **grinding agent,** being an artificial corundum or emery (the basis of which is alumina).

Another curious application of alumina is the **manufacture of artificial rubies and sapphires,** which at the present time has become a considerable industry. This is discussed in the article on **The Artificial Gem Industry,** p. 63. These hard artificial gems are used in watches, instruments, balances, and other kinds of delicate mechanism, where hard, unwearable, smooth surfaces are necessary.

Manufacture of Aluminium Sulphate, $Al_2(SO_4)_2 . 18H_2O$.—The most important raw material for the manufacture of aluminium sulphate is **Bauxite** (p. 49); it is, however, also manufactured from **Kaolin** (china clay) and from **Cryolite** (see p. 51).

Manufacture from Bauxite.—The bauxite (or cryolite) is calcined with soda ash (sodium carbonate) as described on p. 49, the product is lixiviated with water, and from the solution of sodium aluminate nearly pure aluminium hydroxide is precipitated by CO_2 as described on p. 50. The process adopted when cryolite is used as the starting product is described on p. 51.

The filtered and washed $Al(OH)_3$ is next mixed with sulphuric acid of 58°-66° Bé. (133°-167° Tw.), when heat is evolved and the product dissolves to form aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, thus:—

$$2Al(OH)_3 + 3H_2O = 2Al_2(SO_4)_3 + 3H_2O.$$

After cooling, the product sets to a solid glass-like mass, having a porous structure and containing about 60 per cent. $Al_2(SO_4)_2$.

The exact procedure differs in different works. As a rule, however, excess of acid is avoided, the proportion of Al_2O_3 to H_2SO_4 being from 1 : 2.8 or 2.9, against 1 : 3 as required for the compound $Al_2(SO_4)_3$. It is most important that the aluminium hydroxide and the sulphuric acid should be almost totally free from iron, as the presence of only traces of iron in the resulting aluminium sulphate greatly diminishes its value for certain technical purposes. The action which takes place is at first vigorous, the mixture foaming and frothing up. However, as soon as the process is completed this foaming action immediately ceases. The liquid mass is allowed to solidify in flat pans, some 6 ft. long, 5 ft. wide, and 8 in. deep. These pans are covered with lead, and during the solidifying process the mass is often kept continually stirred with wooden shovels, when it finally sets to a number of lumps, each about the size of a hen's egg. The product is then packed into casks.

In some works the hot fluid mass is run into leaden channels, and just before solidification a number of partitions are placed at intervals down the channel, so that when the mass finally sets a number of equal sized blocks, about the size of half a brick, are produced.

The product thus produced is now often almost entirely iron-free. It usually contains a small amount of sodium sulphate, Na_2SO_4 (produced by the action of the sulphuric acid on a little unchanged sodium carbonate, etc., contained in the precipitated aluminium hydroxide), and also a little free sulphuric acid, so that the product has an acid reaction. The presence of the sodium sulphate does not, as a rule, hinder in any way the technical applications of the aluminium sulphate. The acid reaction cannot be destroyed by adding excess of aluminium hydroxide, as the excess does not dissolve.

The properly manufactured product contains 14.3-14.5 Al_2O_3; 33.7 per cent. SO_3; 0.60 per cent. Na_2SO_4; under 0.02 per cent. Fe_2O_3; insoluble residue, 0.5 per cent.; H_2O, 50.68 per cent. (see Jurisch, *Chem. Industrie*, 1894, **17**, 92). This product is so pure that in general it can be directly used instead of alum as a mordant in the dyeing and colour printing industry. In some delicate dyeing operations even so small an amount of iron as 0.001 per cent. exerts a deleterious effect. For sizing paper, 0.01 per cent. of iron is allowable.

Where the presence of iron does not greatly affect the use of the product, sometimes aluminium sulphate is manufactured from bauxite by **the acid process.**

Here the bauxite is treated with dilute sulphuric acid of 45°-52° Bé. (or 90°-112° Tw.) (stronger acid than this being less effective), and the mixture is warmed by means of live steam until the acid is neutralised.

The previously calcined and finely ground bauxite is run through a manhole into a large cast-iron boiler, lined internally with lead and stoneware, which contains the requisite amount of 45°-52° Bé. (90°-112° Tw.) sulphuric acid, heated by indirect steam to 90°-100° C. A violent action soon takes place, and the pressure inside the boiler sometimes rises to 4 atmos. After ten to fifteen minutes the action is completed, and the pressure gradually sinks. By opening a valve the pressure is reduced to atmospheric, the manhole is opened, the pasty mass is diluted until a concentration of 29°-31° Bé. is attained, and the liquid mass run out into tall settling tanks, settled for four days, and the clear solution run off into leaden concentrating pans and concentrated until 42° Bé. is reached, when the liquid is run into small crystallising pans and is allowed to crystallise. The solid cakes thus obtained are subjected to a hydraulic pressure of 300 or more atmos. (whereby iron-containing mother liquors, etc., are pressed out), and the hard white cakes of aluminium sulphate thus obtained, containing less than 0.05 per cent. iron, are sold to paper manufacturers for sizing purposes.

The insoluble residues in the clearing tanks are technically nearly worthless at present. They are washed with water and then thrown away; the aqueous washings are worked up for **alum** as described below.

The great disadvantage of the acid process is the fact that much iron is taken up from the bauxite, so that in general the product can only be used for sizing paper and similar products, where the presence of some iron, *e.g.*, 0.01-0.02 per cent., does not matter. For dyeing purposes, where even a trace of iron, *e.g.*, so little as 0.001 per cent., often spoils the colour effect, it cannot be used, and so the alkaline process of manufacture before described is used for preparing the pure product.

For example, one process (English Patent, 5,579, 1881, Fahlberg & Semple) consists in stirring into the paste from the sulphuric acid a little lead peroxide, PbO_2. The iron is precipitated as $Fe_2O_3.PbO_2$. This remains behind in the insoluble residues of the settling tank. The liquors are then worked up as previously described. Spence oxidises the iron with MnO_2 (English Patent, 3,835, 1882).

Another successful process is to precipitate the iron as **Prussian Blue.** The clear liquor, as it comes from the settling tanks, is first titrated with permanganate, and the amount of ferrous iron in it is exactly estimated. Next the theoretical amount of bleaching powder is run in in order to just oxidise all the iron to the ferric state. The excess of chlorine must be completely removed by blowing air through the liquor. Next ferrocyanide is run in very carefully in the exact amount necessary to precipitate all the iron present as Prussian blue.

The liquid is now carefully filtered under its own pressure through a filter press provided with the finest Nessel filter cloths, which retain most of the Prussian blue. The first portions of the fluid, however, come through turbid, and the liquid is rendered perfectly clear by forcing it once more, but now under 4 atmos. pressure, through a filter composed of twenty or thirty porous plates of calcined magnesia, mounted one behind the other in an enamelled vessel.

By reversing the direction of the entering liquid these plates can be washed free from the clogging Prussian blue.

More recently the liquid has been freed from Prussian blue by sending it through centrifugal machines provided with very fine filtering cloths.

The perfectly clear liquid is now concentrated from 42°-52° Bé. in leaden pans, and allowed to solidify as above described. This product contains only 0.0005 per cent. iron oxide; bad samples sometimes contain 0.01 per cent. Fe_2O_3.

The separated Prussian blue, after washing by boiling with water and pressing, is converted into ferrocyanide by heating with alkalis, and so is used over again.

Manufacture of Aluminium Sulphate from China Clay

White china clay, $Al_2O_3.2SiO_2.2H_2O$, when pure, contains 39.2 per cent. Al_2O_3. Treated with conc. H_2SO_4 the Al_2O_3 is dissolved as $Al_2(SO_4)_3$, while the SiO_2 remains behind insoluble. The clay is reduced to a fine powder and calcined, when a loss of weight of 20-25 per cent. occurs, owing to loss of water.

The calcined clay is now treated in a lead-lined wooden vat with somewhat less conc. sulphuric acid (96° Tw., 60° Bé.) than suffices to dissolve all the Al_2O_3. A vigorous action takes place, and after fifteen to twenty minutes of continual stirring, the mass is run into lead-lined wooden waggons with removable sides, in which the action continues for some time. Finally the mass solidifies, and is then reduced by cutting with a heavy knife to a coarse powder.

This product, known as **"alum cake,"** has the average composition: soluble Al_2O_3, 12-13.5 per cent.; Fe_2O_3, 0.10-0.25 per cent.; combined SO_3, 29-32 per cent.; free SO_3, 0.5-1 per cent.; insoluble matter, 20-27 per cent.

By this process some 60 per cent. of the Al_2O_3 originally present in the clay is converted into $Al_2(SO_4)_3$.

"White Sulphate of Alumina" is prepared from the crude "alum cake" by lixiviating the latter with hot water (heated by live steam) in lead-lined wooden tanks. After settling, the clear fluid is decanted into lead-lined evaporators and concentrated to a density of 112° Tw. (52° Bé.). It is then run into a series of shallow tiled troughs, where it solidifies to a crystalline mass.

This product contains 0.25 per cent. Fe_2O_3 and 14 per cent. Al_2O_3, and is largely used for sizing paper (see **Martin's** "Industrial Chemistry: Organic").

In this process, of 35 per cent. Al_2O_3 of the clay no less than 15 per cent. remains behind in the residue of SiO_2.

Properties of Aluminium Sulphate.—The substance is variously given the formula $Al_2(SO_4)_3.18H_2O$, and $Al_2(SO_4)_3.20H_2O$. It crystallises in white, pearly tablets, and is very soluble in water. On heating it melts in its water of crystallisation, and then swells up, the anhydrous salt only slowly dissolving again in water. At a red heat it is decomposed into Al_2O_3.

The following figures give the weight of salt which dissolves in 100 parts H_2O:—

Temperature - -	0°	10°	20°	50°	100°
Crystallised salt - -	86.8	95.8	107.3	201.4	1132.0
Anhydrous salt - -	31.3	33.5	36.1	52.1	89.1

The following table gives the specific gravities of solutions of aluminium sulphate of various strengths:—

Per cent. $Al_2(SO_4)_3$.	Sp. Gr.	Per cent. $Al_2(SO_4)_3$.	Sp. Gr.	Per cent. $Al_2(SO_4)_3$.	Sp. Gr.
1 - -	1.017	10 - -	1.107	19 - -	1.197
2 - -	1.027	11 - -	1.117	20 - -	1.207
3 - -	1.037	12 - -	1.127	21 - -	1.217
4 - -	1.047	13 - -	1.137	22 - -	1.227
5 - -	1.057	14 - -	1.147	23 - -	1.237
6 - -	1.067	15 - -	1.157	24 - -	1.247
7 - -	1.077	16 - -	1.167	25 - -	1.257
8 - -	1.087	17 - -	1.177		
9 - -	1.097	18 - -	1.188		

The substance is insoluble in absolute alcohol and free H_2SO_4, etc., and can be removed by precipitating the substance from aqueous solution with much alcohol.

Alum, $K_2SO_4.Al_2(SO_4)_2.24H_2O$.—The most important raw material for the manufacture of alum is **Bauxite**; of lesser importance is **Alunite** (alumstone) and Kaolin. Some alum and aluminium sulphate is also produced from **Kryolite**. The manufacture from black bituminous, aluminiferous shale has now, to a large extent, been given up.

Alunite, Alumstone, is the oldest known raw material for the manufacture of alum and other aluminium compounds. It is a basic potassium aluminium sulphate, of formula $K(AlO)_3(SO_4)_2.3H_2O$, and is a volcanic product, being produced by the combined action of SO_2 and steam on lava.

It occurs in China (where an "alum mountain, 1,900 ft. high, with a circumference at the base of 10 miles," is said to occur) (see "U.S. Cons. Report," 1903), Hungary, Greece, and Italy.

The best known source is at **Civita Vecchia**, in Italy. This has been known and worked for centuries, and is still worked at the present time for producing "Roman alum."

The native alunite cannot be directly extracted with water, because it consists of a **basic** alum insoluble in water. It must first be heated to a high temperature, when it loses its hydrated water, crumbles, and becomes soluble in water.

The method of procedure is as follows:—The alunite is first calcined at 600°, and then broken up and exposed to the action of the atmosphere. Next, the mineral is extracted with water, whereby alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, passes into solution, while unchanged clay, alumina, iron oxide, etc., remain behind.

On concentrating the solution the alum crystallises out in cubes. This alum, being almost entirely free from iron, was at one time a valuable product.

The modern method of working alunite for alum is to treat the calcined and finely powdered mineral with sulphuric acid and allow the solution thus obtained to crystallise.

There first crystallises out alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, and the mother liquors from this, when further concentrated, yield a crystallised mass of aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, which is much more soluble and much more difficult to obtain pure than alum.

Manufacture of Alum from Bauxite or Kaolin.—Aluminium sulphate solution is first prepared by treating the bauxite or kaolin with sulphuric acid according to the acid process described on pp. 52-53.

To the concentrated hot solution of aluminium sulphate there is now added potassium sulphate, and the liquid is vigorously stirred. On cooling, the moderately soluble potassium alum separates as a fine crystalline mass:—

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = K_2SO_4.Al_2(SO_4)_3 24H_2O.$$

The formation of large crystals is avoided by stirring during the precipitation. Large crystals enclose mother liquor, and so their formation is avoided.

Sometimes instead of potassium sulphate the cheaper potassium chloride is used, when the following action takes place:—

$$4Al_2(SO_4)_3 + 6KCl = 3Al_2(SO_4)_2.K_2SO_4 + 2AlCl_3.$$

The aluminium chloride remains in solution, and so is lost for the formation of alum.

The alum crystals are separated from the greenish-coloured iron-containing mother liquors, and are well washed with water and again dissolved in hot water and crystallised therefrom, after first making a solution of sp. gr. 1.5.

On account of its moderate solubility in cold water alum can be easily prepared almost quite iron-free, and so is used for purposes where the absence of iron is necessary.

Properties of Potassium Alum, $K_2SO_4Al_2(SO_4)_3.24H_2O$.—The body is only moderately soluble in cold water: 100 parts of water dissolve:—

Temperature :—	0° C.	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
$K_2SO_4.Al(SO_4)_3.24H_2O$ dissolved :—	3.9	9.5	15.1	22.0	31.0	44.1	66.6	90.7	124.5	209.3	357.5

The specific gravity of the aqueous solution at 17.5° C. is :—

Per cent. alum - - -	4	8	12	13
Specific gravity - - -	1.0205	1.0415	1.0635	1.0690

The aqueous solution is acid in reaction, dissolving iron and zinc with evolution of hydrogen. It boils at 111.9° C., is insoluble in alcohol; heated, it melts in its water of crystallisation at 92.5° C.; ignited, it loses its water of crystallisation and also sulphuric acid, and goes into "burnt alum."

The ordinary alum crystallises in octahedra, but in a neutral solution (to which alkali carbonate, lime, caustic potash, or soda has been added) the substance crystallises out below 45° in cubes. Exposed to the air, alum loses part of its water of crystallisation.

In the technical application of alum the chemically active part is simply the aluminium sulphate, $Al_2(SO_4)_3$, and so within recent years the manufacture of aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, has taken place on an increasing scale.

Were it possible to obtain aluminium sulphate as pure as alum, there is little doubt that alum would be completely displaced by it.

However, aluminium sulphate is very soluble in water (soluble in its own weight of water) and crystallises with difficulty, and is difficult to free from iron and free H_2SO_4, consequently for all purposes where a pure salt is necessary alum is superior to aluminium sulphate.

Ammonium alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$, is prepared in a manner precisely similar to potassium alum, merely by adding ammonium sulphate to a solution of aluminium sulphate.

Since ammonium alum is only very slightly more soluble in water than potassium alum, it can also, like this latter, be easily prepared in a pure state by crystallisation.

100 parts of water dissolve :—

Temperature -	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Ammonium alum -	5.2	9.1	13.6	19.3	27.3	36.5	51.3	72.0	103	188	422

Ignited it leaves a residue of pure alumina, Al_2O_3.

The crystals frequently have an amethyst tint (possibly due to traces of iron and chromium), although containing less than 0.001 per cent. of iron.

Since the introduction of cheap potassium chloride from Stassfurt, ammonium alum is no longer manufactured to the same extent in England as it was formerly.

Sodium alum, $Na_2SO_4.Al_2(SO_4)_3.24H_2O$, is also prepared on a large scale. It is more soluble in water than potassium alum, and is also cheaper. It is, however, more difficult to prepare pure than either potassium or ammonium alum, on account of its great solubility, 100 parts of water dissolving 51 parts sodium alum at 16° C. Two other alums, which are prepared on a large scale, are **potassium chrome alum,** $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, and **ammonium iron alum,** $(NH_4)_2Fe_2(SO_4)_3.24H_2O$.

Some other Salts of Alumina

Aluminium acetate, prepared in aqueous solution by treating aluminium sulphate (or alum) solution with lead acetate ($3PbAc_2 + Al_2(SO_4)_3 = PbSO_4 + 2AlAc_3$), or by dissolving precipitated aluminium hydroxide, $Al(OH)_3$, in acetic acid, finds fairly extensive use as a mordant in dyeing and colour printing on cloth.

Aluminium chloride, $AlCl_3$, is obtained technically by dissolving precipitated aluminium hydroxide, $Al(OH)_3$, in HCl. It is used for carbonising wool (see **Martin's** "Industrial Chemistry: Organic").

Solid sodium aluminate, $Al(ONa)_3$, is sometimes obtained from bauxite or cryolite, as above described (see pp. 49, 51), by heating with soda or caustic soda, extracting with water, and concentrating the liquid when it is obtained as a white, easily soluble mass. Its solution is decomposed by atmospheric CO_2 (or even on long standing by water), giving a precipitate of $Al(OH)_3$. Consequently, when the powder is exposed to air for any length of time, it yields turbid solutions.

It finds use as a mordant in dyeing and cloth printing, and in the preparation of certain paints. It is also sometimes used in sizing paper, for the manufacture of aluminium soaps (substitute for alum), for hardening plaster of Paris and similar stony compositions, and for saponifying fats in candle manufacture.

Technical Uses of Salts of Alumina.—Both alum and aluminium sulphate find extensive use as **mordants** for cotton and wool. The salts used for this pur pose must be almost iron-free—0.01-0.001 per cent. of iron often rendering these products useless for such dyes as alizarin. This high degree of purity was, until recently, only attainable with alum, since aluminium sulphate is very difficult to crystallise and purify from the iron-containing mother liquors. A still greater quantity of alum (and still more aluminium sulphate) is used for **sizing paper** (see **Martin's** "Industrial Chemistry: Organic"), a mixture of resin soap (rosin partly dissolved in NaOH), starch, and aluminium sulphate being added to the paper pulp, and so forms an adherent precipitate of aluminium rosenate, which causes the fibres to adhere together and prevents ink sinking into the paper.

Aluminium salts also find extensive use in making cloth **waterproof**, the method being explained in **Martin's** "Industrial Chemistry: Organic." Wood is made **fireproof** by impregnating with aluminium sulphate.

Aluminium soaps (made by treating ordinary soaps with aluminium acetate or sulphate) find a variety of uses, one of which is the cementing together of sandstone to form solid blocks. The aluminium soap is sometimes sold for this purpose under the name "Testalin."

Both **alum** and **aluminium sulphate** are used in tanning leather (see **Martin's** "Industrial Chemistry: Organic"). Another use of aluminium sulphate is the clearage of sewage water. Water is treated with this substance, together with lime-water, when a gelatinous precipitate of aluminium hydroxide brings down with it any suspended organic matter (see **Martin's** "Industrial Chemistry: Inorganic," Vol. I.).

Statistics

The following statistics relating to world production of bauxite and aluminium are abstracted from "The Mineral Industry," Statistical Summary, Imperial Institute, 1938–49:—

WORLD PRODUCTION OF BAUXITE
(Long Tons)

	1938.	1947.
British Guiana (60 per cent. or more alumina)	447,370	1,358,929
Malayan Union	55,081	...
Australia	1,764	4.878
France	673,020	668,500
Greece	177,045	Inf. not available
Hungary	532,177	279,100
Italy	355,138	165,070
U.S.S.R. (estimated)	250,000	450,000
Yugoslavia	398,180	Inf. not available
United States	310,916	1,215,308
Dutch Guiana	371,633	1,711,670
Netherlands East Indies	241,479	...
World Total	3,900,000	6,170,000 (estimated)

[TABLE

ESTIMATED WORLD PRODUCTION OF ALUMINIUM
(Long Tons)

	1938.	1947.
United Kingdom	23,000	28,940
Canada	63,575	267,023
India	..	Inf. not available
France	44,600	52,557
Germany	158,682	Inf. not available
Italy	25,360	24,668
Norway	28,576	21,382
Switzerland	26,100	20,000
U.S.S.R.	50,000	Inf. not available
United States	128,072	510,491
Japan	16,464	2,657
World Total	587,000	1,060,000

REFERENCES

(1) B.I.O.S. 308, Production of Aluminium in Italy (1948).
(2) B.I.O.S. JAP PR 1503. Japanese Metallurgy. Recovery of Aluminium from Clay and Shale (1948).
(3) B.I.O.S./JAP/PR/902, The Raw Aluminium Industry of Japan (1947).
(4) C.I.O.S. XXXII-59. Aluminium and Magnesium Production and Fabrication (1947).
(5) F.I.A.T. 501, German Aluminium and Magnesium Industries (1946).
(6) F.I.A.T. 993, The Aluminium Reduction Industry in Germany (1947).
(7) F.I.A.T. 997, Review of Recent German Developments in Aluminium Refining (1947).
(8) F.I.A.T. 731. Technology of Aluminium and Aluminium Alloys—Production in Germany (1946).
(9) J. R. Callaham, *Chem. Met. Eng.*, **52, 12,** 108 (1945).
(10) E. P. Flint *et. al., J. Res. Nat. Bur. Std.,* **36**, 63 (1946).

SECTION LVI

THE ARTIFICIAL ZEOLITE OR PERMUTITE INDUSTRY

By Geoffrey Martin, D.Sc., Ph.D.

Revised by Wilfrid Francis

LITERATURE

R. Gans.—*Chem. Ind.*, 32, 197 (1909); *Chem. Zentr.*, 52 (1908); *Chem. Zentr.*, I. 2031 (1909).

S. J. Hopkins.—*Manuf. Chem.*, **17**, 285 (1946.)

M. H. Hey.—*Mining Magazine*, **22**, 422 (1930).

A. R. Martin.—*C.T.J.*, **86**, 29 (1930).

J. G. Walker.—*Chem. and Ind.*, **44**, 695 (1948).

The zeolites are a large class of naturally occurring hydrated aluminium silicates containing alkali or alkaline earth metals. A few of the more important are:—

Natrolite - - -	$Na_2O.Al_2O_3.3SiO_2.2H_2O$.
Analcite - - -	$Na_2O.Al_2O_3.4SiO_2.2H_2O$.
Chabazite - - -	$CaO.Al_2O_3.4SiO_2.6H_2O$.
Stilbite - - -	$CaO.Al_2O_3.6SiO_2.6H_2O$.

They play an important part in soils, by retaining in a readily soluble form the alkalis set free on the weathering of felspar. They can be artificially synthesised, and within the last few years they have become of considerable industrial importance owing to R. Gans' discoveries that they contain alkali or alkaline earth metals which, when brought into contact with various solutions of metallic salts, are interchanged for the metal from the salt solution, the alkali or alkaline earth metal in the zeolite itself going into solution in the salt.

The name given to the artificially made zeolite is "**Permutite**," of which many different varieties exist, according to the nature of the bases employed in their manufacture.

Manufacture.—The permutites are made by igniting together china clay (aluminium silicates) and (sometimes) quartz or sand with the alkali carbonates. The melt is extracted with water, and the residual permutite is left as a granular mass. This must be porous if a high degree of reactivity is necessary—a condition which is attained by the presence of potassium as one of the bases.

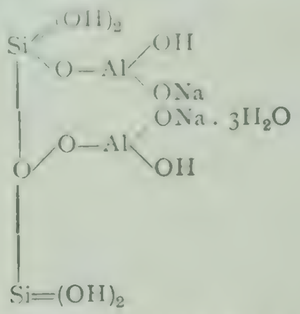
R. Gans, in his D.R. Patent, 174,097, of 12th Jan. 1905, manufactures zeolites by allowing an alkali aluminate, free from uncombined alkali, to act on hydrated silicic acid. Heat is employed to complete the union, and then calcium chloride, $CaCl_2$, solution is added. The alkali is thereby exchanged for the calcium. The zeolites made by this process have the formulæ of the natural zeolites, *e.g.*, $CaO.Al_2O_3.6SiO_2+6H_2O$, or $CaO.Al_2O_34SiO_2+8H_2O$.

J. D. Riedel, in his D.R. Patent, 186,630, of 24th Feb. 1906, manufactures zeolites by fusing together 3 parts of kaolin, 6 parts of quartz, and 12 parts of sodium carbonate. Excess of alkali must be carefully avoided. There results $Al_2O_3+10Na_2O+10SiO_2$.

In his later patent, D.R.P., 200,931, of 11th Oct. 1907, Riedel replaces the sodium carbonate by a mixture of the cheaper sodium sulphate and coal. On extracting with water a crystalline alumino-silicate passes into solution.

In general, the greater the percentage of sodium or potassium present in the molecule, the greater is their capacity of interchanging their bases. According to Gans, in general to every 1 molecule Al_2O_3 present, we must have present 1 molecule Na_2O or K_2O. The chemical formula of a typical zeolite is given by Gans as $Al_2O_3.Na_2O.2SiO_2 + 6H_2O$.

These artificial aluminium silicates possess properties only found to a very minute degree in similar natural silicates. This peculiar behaviour led Dr Gans to the conclusion that in the artificial product the sodium or potassium are joined to the silicon through the medium of aluminium, while in the natural silicates the base was attached in the usual way, the atoms of hydrogen being replaced by the metals. The graphic formula of a simple artificial aluminium silicate of empirical formula, $Na_2O.Al_2O_3.2SiO_2.6H_2O$, would then be as follows :—



A sodium zeolite is now made on a large scale, and put on the market under the name of "Sodium Permutite." It is used either as such, or is converted into other permutites containing basic components other than sodium, and the uses to which it has been technically subjected are as follows :—

(1) **The removal of calcium and magnesium salts from water.**—*E.g.*, if it is desired to remove $CaCl_2$ from water, the water is sent through a granular layer of sodium permutite some 60-100 cm. high, when a calcium permutite is formed, and sodium chloride passes in solution, thus—

$$\underset{\text{Sodium permutite.}}{NaO.Al_2O_3.2SiO_2} + CaCl_2 = \underset{\text{Calcium permutite.}}{CaO.Al_2O_3.2SiO_2} + 2NaCl.$$

In order to regenerate the sodium permutite when exhausted, a concentrated NaCl solution is led through the layer of permutite, when the calcium permutite formed is decomposed according to the equation :—

$$\underset{\text{Calcium permutite.}}{CaO.Al_2O_3.2SiO_2} + 2NaCl = \underset{\text{Sodium permutite.}}{Na_2O.Al_2O_3.2SiO2} + CaCl_2.$$

Thus calcium, magnesium, and similar salts can be easily removed from water, the calcium or magnesium replacing the sodium of the permutite, and sodium salts being formed in solution, and the process has already attained considerable technical importance as a water-softening process (see this work, Vol. I., under **Water**).

(2) **Removal of sodium and potassium salts from water.**—For this purpose the water is sent through a calcium permutite. *E.g.*, if it is desired to free water from Na_2CO_3, the water is filtered through calcium permutite, when the following change takes place :—

$$CaO.Al_2O_3.2SiO_2 + Na_2CO_3 = Na_2O.Al_2O_3.2SiO_2 + CaCO_3.$$

In the sugar industry Harms and Rümpler have used a similar process for clearing the juice and withdrawing potassium for sodium in the salts contained therein, thereby attaining a better taste in the molasses.

The calcium permutite of Gans removes from the sugar, syrup, and molasses not only the greater part of the potash, but also much sodium, by exchanging these bases for lime. The hot molasses can be filtered without dilution with water, so that reconcentration is avoided. In order to exchange the potash for an equivalent of sodium, the molasses is sent through a sodium permutite, when the potassium permutite is formed, while the sodium takes its place in solution. Molasses containing only sodium are stated to be much better than those which contain either potassium or lime. See **Siedler**, *loc. cit.*

(3) **Removal of manganese and iron from water.**—For the removal of manganese a manganese permutite is first made from calcium permutite and manganese chloride, thus :—

$$\underset{\text{Calcium permutite.}}{CaO.Al_2O_3.2SiO_2} + \underset{\text{Manganese chloride.}}{MnCl_2} = \underset{\text{Manganese permutite.}}{MnO.Al_2O_3.2SiO_2} + \underset{\text{Calcium chloride.}}{CaCl_2}.$$

Next, the manganese radicle in the manganese permutite is converted into the heptoxide by treating with calcium or potassium permanganate :—

$$MnO.Al_2O_3.2SiO_2 + Ca(MnO_4)_2 = CaO.Al_2O_3.2SiO_2 + MnO.Mn_2O_7.$$

The $MnO.Mn_2O_7$ is precipitated on and in the zeolith particles, and exercises an oxidising action on the lower oxides of manganese contained in the water, being itself reduced to lower stages of oxidation. Owing to this oxidising action the manganese contents of the water is completely precipitated as MnO_2. For example, if the manganese is present in water as a bicarbonate, $Mn(HCO_3)_2$, we get the following action taking place:—

$$2Mn(HCO_3)_2 + MnO.Mn_2O_7 + CaO.Al_2O_3.2SiO_2 = 5MnO2 + 2H_2O + 2CO_2 + CaO.Al_2O_3.2SiO_2.$$

As soon as the manganese heptoxide has lost all its available oxygen its power of removing manganese from water is exhausted. This may be regenerated merely by retreating the permutite with calcium or potassium permanganate. The manganese mud formed which remains on the filter increases its efficiency.

Use is made of their reactions in sterilising water. First of all, the germs are killed by adding to the water some calcium or potassium permanganate. Next, the sterilised water is filtered through a manganese permutite, whereby all the permanganate and other manganese salts are removed. See this work, Vol. I., under **Water.**

The complete removal of iron from water is similarly effected by means of a manganese permutite. The iron is removed completely from the water, and this matter of de-ironising water is the most complete and efficient yet introduced into industry.

The action in removing the iron is probably catalytic. Under the influence of the manganese heptoxide and monoxide on the surface of the zeolite, the oxygen in the water oxidises the iron completely and quantitatively. It is thrown down and retained as oxide by the zeolite.

(4) **Removal of free alkali from water.**—The permutites possess the capacity of absorbing free alkalis from aqueous solution. By treating the zeolite with weak acids the absorbed alkali can be given up once more.

(5) **Preparation of salts of different bases by exchange.**—It is possible to extract a salt out of a dilute solution by filtering through a suitable permutite, and next, by suitable treatment, obtain it again in a concentrated form. For example, by passing a solution of potassium chlorate or perchlorate through an ammonium permutite, we get formed ammonium chlorate or ammonium perchlorate. By filtering ammonium carbonate through potassium permutite, potassium carbonate is obtained, and so on.

The use of this in recovering valuable salts escaping in waste liquors from factories as by-products will be obvious. It is possible that this process may have some value in quantitatively determining the amount of calcium, etc., in very dilute solutions.

(6) **Precipitation of gold from solution.**—The sodium base of sodium permutite is exchanged for ferrous or stannous oxide, and the gold-containing solution is filtered through it.

Gold from even extremely dilute solutions is precipitated in the zeolitic mass as purple of Cassius.

The manufacture and use of artificial zeolites (permutites) are protected by **the patents of the firm of J. D. Riedel, A.G., Berlin.**

Complete Exchange Zeolites (Carbonaceous Zeolites)

Modern synthetic zeolites can exchange hydrogen ions for calcium or magnesium ions. This development enables water to be completely demineralised by exchange and absorption processes instead of being merely softened, as with the sodium zeolite, base exchange minerals. This process is fully described in Martin, Inorganic, Vol. I., Section XVI., and the application to boiler feed water conditioning in "Boiler House and Power Station Chemistry" by W. Francis (London, 1948).

The exchange and absorption materials used in these processes are sometimes sulphonated compounds, derived from selected coals or resins by heating with concentrated or fuming sulphuric acids at temperatures in excess of 100° C. The following references relate to papers and patents describing the preparation and properties of carbonaceous zeolites:—

S. J. Broderick and D. Bogard, "Cation Exchangers from Coal and Coal Refuse," U.S. Bur. Mines, Report of Investigations, No. 3559; *Coke*, **3**, 286 (1941).

S. J. Broderick and D. Bogard, "Carbonaceous Zeolites from Bituminous Coal," *Ind. Eng. Chem.*, **33**, 1291–6 (1941).

R. P. Donnelly, "Use of 'Organolites' in Water Treatment," *Colliery Eng.*, **20**, 122–125 (1943).

Permutit Co., "Ion Exchange Materials." (U.S.P. 2,260,971. 1941.)

I. G. Farbenindustrie, A. G., "Manufacture of Absorptive Materials, especially Applicable for Cation Exchange." (B.P. 492,316, 1938.)

United Water Softeners Ltd., "Improvements relating to the Manufacture of Ion Exchange Materials." (B.P. 450,574, 1936.)

SECTION LVII

THE ARTIFICIAL GEM INDUSTRY

By Geoffrey Martin, D.Sc., Ph.D.
Revised by Wilfrid Francis

LITERATURE

A. Verneuil.—"Production artificielle du rubis par fusion." *Compt. rend.*, 135, 791 (1902); *ibid.*, 147, 933 (1908); *Ann. Chem. Phys.*, 3, 20, [8] (1904).
J. Boyer.—"La Synthèse des pierres precieuses." Paris, 1909.
Noël Heaton.—"Artificial Precious Stones," *Chem. World*, I., 79 (1912).
F. Krauss.—"Synthetische Edelsteine." Berlin, 1929.
H. Michel.—"Die Künstliche Edelsteine." Leipzig, 1926.
P. Goodzinski.—"Diamond and Gem Stone Industrial Production." 1942.
B.I.O.S. 1448.—German Industrial Diamond Industry. 1947.

The following table shows the composition of the principal precious stones :—

	Species.	Variety.	Composition.
Element	Diamond	...	Carbon.
Oxides	Corundum	Ruby Sapphire Oriental amethyst, etc.	Al_2O_3.
	Quartz	Rock crystal Cairngorm Amethyst	SiO_2.
Albuminates	Spinel	Balas ruby, etc.	Magnesium aluminate, $MgAl_2O_4$.
	Chrysoberyl	Alexandrite Cymophane	Beryllium aluminate.
Silicates	Beryl	Emerald Aquamarine	Beryllium aluminium silicate.
	Garnet	Pyrope	Magnesium aluminium silicate.
		Hessonite	Calcium ,, ,,
		Almandine	Iron ,, ,,
		Demantoid, etc.	Calcium iron silicate.
	Olivene	(Peridot)	Magnesium iron silicate.
	Sphene	...	Calcium titanium ,,
	Spogumene	(Kunzite)	Lithium aluminium silicate.
	Topaz	...	Aluminium hydroxy-fluo-silicate.
	Tourmaline	...	Alkali-calcium aluminium silicate.
	Zircon	Hyacinth Jargoon	Zirconium silicate.
	Turquoise	...	Hydrated aluminium phosphate.
	Pearl	...	Calcium carbonate.
	Opal	...	Hydrated silica.

Corundum and spinel are the main gem stones which have been produced artificially of a size and quality suitable for jewellery. Moissan has produced microscopic diamonds (see Moissan, "The Electric Furnace," 1904), but valueless as gems.

Artificial turquoises have been made for thirty years from aluminium phosphate containing water and a trace of copper to give a blue colour to the product.

"**Reconstituted rubies**" consist of splinters of rubies cemented together by a lead-containing flux.

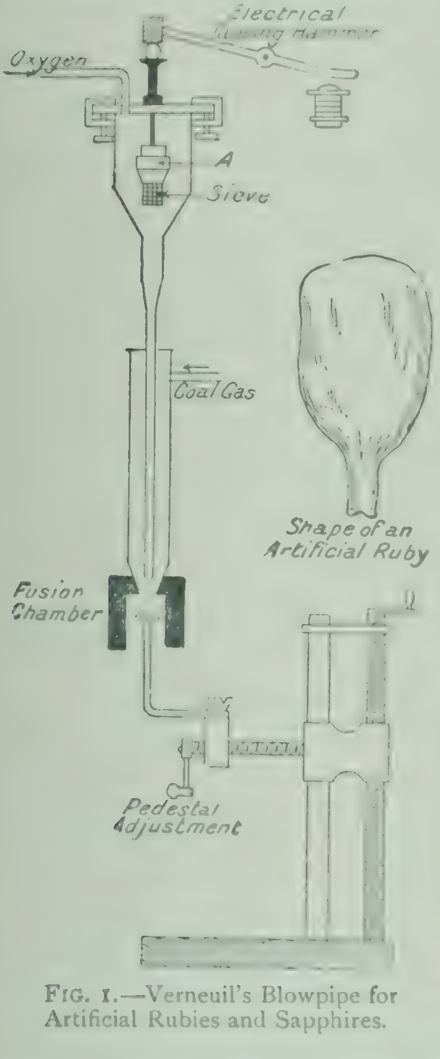


FIG. 1.—Verneuil's Blowpipe for Artificial Rubies and Sapphires.

Genuine rubies, under the name "rubis scientifiques," were made by Fremy in 1891, by heating to 1,500° in a porous crucible a mixture of pure precipitated Al_2O_3, with a little BaF_2 (or CaF_2), K_2CO_3, and 2-5 per cent. potassium bichromate. The moist gases of the furnace caused the liberation of HF, and this, combined with water vapour, caused the crystallisation of the alumina into small rubies. However, in 1902, A. Verneuil, of Paris, made his "rubis synthetiques," which have since attained considerable importance, his factory producing annually some 5,000,000 carats of precious stones (1,000 kg.). The main process is briefly this:—

Pure iron-free ammonium alum,

$$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O,$$

is mixed with a little chrome alum,

$$(NH_4)_2SO_4.Cr_2(SO_4)_3.24H_2O,$$

and the whole precipitated in warm aqueous solution by means of ammonia. A mixture of $Al(OH)_3$ and $Cr(OH)_3$ ($2\frac{1}{3}$ per cent. Cr_2O_3 gives the best colour) is thus obtained.

The product is dried in the air, dehydrated at a bright red heat, and then the fine powder thus obtained is fused into a coherent mass in a special vertically placed reducing blowpipe flame, the flame playing downwards (see Fig. 1). Into this flame, from a receptacle A, the fine powder is allowed to steadily fall in a stream from a platinum sieve situated in a widening of the oxygen tube. A steady automatic shaking of this sieve by means of a tapping hammer, worked by an electromagnet, ensures that a steady rain of powder falls downwards continuously into the flame, and cools as a little cone of fused pure alumina just below the flame. First of all a little rod of fused alumina is formed, which later assumes the form of a drop, and finally acquires the form of an inverted bottle. The drop must finally be cautiously cooled (otherwise it may crack), and is then ground down. It is stated that it is by no means unusual to form true artificial rubies of some 50-80 carats (10 g.) which, after cutting, form 12 carat rubies of a fine red colour. The uncut stones have a value under one shilling a carat. The sp. gr. (3.98-4.0), hardness, optical properties, etc., agree with the natural rubies.

Omission of the chromium leads to the formation of "**white sapphires**," consisting of pure alumina, Al_2O_3.

Other stones are also made of various colours and qualities, yellow like topaz, violet, amethyst, and also blue like sapphire. Since the blue colour of the sapphire is destroyed by intense heat, the colouring is artificially imparted to these stones by adding a little cobalt salt in the presence of lime or magnesium (otherwise the cobalt is not dissolved by the alumina), when a **blue spinel** ($MgAl_2O_4$) is formed.

True **blue sapphires** are made by Verneuil by adding 0.5 per cent. titanium dioxide, TiO_2, and 1.5 per cent. magnetic oxide of iron, Fe_3O_4; analysis of the resulting sapphire gave Al_2O_3, 99.84 per cent.; TiO_2, 0.11-0.13 per cent.; Fe_2O_3, *trace*; sp. gr. 3.977-4.01.

Most of the other precious stones are either very costly to produce, or else do not possess sufficient value for their artificial production. The Japanese produce a kind of artificial pearl by introducing a mother-of-pearl shape between the shell and mantle of the oyster. The oyster deposits in time a layer of nacre over this. The mass, after removal, is backed with mother-of-pearl. A real artificial pearl or opal has not yet been made. Imitation diamonds, etc., are made from highly refractive lead or other class, called "paste," or "strass." (See this Vol., under **Glass.**)

Other Coloured Stones Based on Corundum

Other coloured stones with corundum as base are formed by the addition of up to 1½ per cent. of various metallic oxides to pure fused aluminium oxide. For example, nickel oxide produces a yellowish stone; nickel and chromium oxides, a yellow-red stone; nickel, iron, and titanium, a green stone; whilst **topaz** is formed by the addition of nickel and manganese oxides. Pure, finely divided alumina, which is used exclusively in the preparation of such artificial gems, is obtained by the thermal decomposition of pure ammonium alum.

Cultured Pearls

Between the two world wars the Japanese built up a large industry in the manufacture of "cultured pearls." These are obtained by placing a small irritant particle within the sensitive outer layers of the pearl oysters. The oysters used are kept in special beds under controlled conditions of growth, and the pearls produced are almost indistinguishable from real pearls. In fact, they are real pearls produced by the artificial stimulation of the pearly oyster.

Imitation Diamonds

These are made from highly refractive lead or other glasses and are called "paste" or "strass." They are, of course, greatly inferior in composition, whereas the artificial corundums and related gems are almost identical with the real stones.

REFERENCES

(1) B.I.O.S. 1515, German Jewellery Industry (1947).
(2) J. Papish and W. J. O'Leary, *Ind. Eng. Chem. An. Ed.*, **3**, 13 (1931).

SECTION LVIII

ALUMINOTHERMICS: "THERMIT" AND ITS APPLICATIONS

By H. Stanley Redgrove, B.Sc. (Lond.), F.C.S.
Revised by Wilfrid Francis

LITERATURE

H. Stanley Redgrove.—"The Goldschmidt Reaction," *Knowledge*, Vol. XXXIV., pp. 249 *et seq.* (London 1911).

J. Bally.—*Rev. de l'aluminium*, **6**, 781 (1929).

K. Goldschmidt.—"Aluminothermie." Leipzig, 1925.

J. D. Edwards, F. C. Frary, and Z. Jeffries.—"Aluminium Products and their Fabrication." New York, 1930.

N. F. Budgen.—"Aluminium and its Alloys." London, 1947.

T. Burchell.—"The Aluminothermic Process: Symposium on the Refining of Non-Ferrous Metals," *J. Inst. Min. and Met.* London, July 1949.

C. H. Herty and G. R. Fitterer.—"Deoxidation of Steel with Aluminium," *Met. Adv. Board* (Pittsburgh), *Bull.* 46 (1929).

A. M. Prentiss.—"Chemicals in War." New York, 1937.

HISTORICAL AND THEORETICAL

If one examines a table of the heats of combustion of the elements, in which the figures given refer in each case to the same weight of oxygen, it will be found that aluminium stands almost highest. It is evident, therefore, that it ought to be possible to obtain a reduction of the oxides of most other elements by means of aluminium.

Early experiments in this field, however, proved very unsatisfactory. The brothers **Tissier**, who attempted the preparation of manganese in this way, did not succeed in getting any reaction, probably because they did not heat their ingredients to a sufficiently high temperature. Other experimenters found that the reaction between aluminium and metallic oxides took place with explosive violence. **L. Frank** and others have succeeded in reducing various oxides and other compounds by heating them with aluminium in the ordinary way; but it is to a discovery made by **Dr Hans Goldschmidt** that all the technological developments of the subject are due.

Goldschmidt required, for the purposes of another experiment, a quantity of pure aluminium sulphide, and after some unsuccessful attempts to prepare this by other methods, attempted the reduction of galena (lead sulphide) by means of aluminium. The ingredients in coarse powder were intimately mixed together and heated in a furnace. A violent reaction took place, with the generation of sufficient heat to render the whole contents of the crucible fluid, and by using a weight of aluminium slightly in excess of that given by the equation,

$$3PbS + 2Al = Al_2S_3 + 3Pb,$$

aluminium sulphide of a very high degree of purity was obtained. The excess of aluminium settled out as a button from the mass of lead (which, owing to its density, sank to the bottom of the crucible), and removed from it various metallic impurities (*e.g.*, silver).

Goldschmidt was thus led to experiment on oxides; and these experiments and those of other investigators show (1) that the reaction between aluminium and metallic oxides will not take place until a certain critical temperature is reached—about 1,050° C. in the case of chromic oxide; and (2) that the reaction once started generates sufficient energy to heat the mixture to a temperature (2,700° C. in the case of ferric oxide) far above this critical temperature. It follows, therefore, that if the reaction can be once started at any point in the mixture, it will spread throughout the whole mass. The case is quite analogous to that of a ball balanced at the top of a hill, which may serve to illustrate the principle involved. Nothing happens so long as sufficient energy to overcome the friction between the surface of the ball and the ground at the top of the hill is not forthcoming; but if this friction is once overcome, the ball will commence to roll down the hill, and will continue until its journey is completed at the bottom. **Goldschmidt** succeeded in producing reactions in the case of mixtures of aluminium and metallic oxides by means of a fuse of aluminium and barium peroxide (which can be ignited by a flaming vesta), or in some cases by means of a burning strip of magnesium ribbon. The reaction can very easily be carried out. All that is necessary is to make an intimate mixture of aluminium and the oxide, both in powder, in a fire-clay crucible, which may be stood inside another crucible to avoid overflowing of the contents in case the first crucible should crack. The reaction is then started by a fuse as described above. It rapidly spreads throughout the mass, the whole contents of the crucible becoming liquid, and the metal sinking to the bottom.

In some cases, by using a weight of metallic oxide slightly in excess of the theoretical, metals of a very high degree of purity, free from carbon, may be obtained. **Goldschmidt** succeeded in producing reactions with oxides of the following metals:—Chromium, manganese, iron, copper, titanium, tungsten, molybdenum, nickel, cobalt, zirconium, vanadium, niobium, tantallum, cerium, thorium, barium, calcium, sodium, potassium, lead, and tin—but the pure metal was not obtained in every case. In some cases, however, such as that of titanic oxide, in which the product is not the pure metal, it is sufficiently pure to serve for the preparation of the chloride. Moreover, by using mixtures of metallic oxides, alloys of desired composition can be obtained.

The reaction in the case of ferric oxide is represented by the following equation:—

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe + 197 \text{ k.cal.}$$

A mixture of ferric oxide (or other oxide of iron) with aluminium, in the right proportion, has very many technological uses, as will appear hereafter, and has been given the registered name of "thermit." Reactions similar to those between aluminium and ferric oxide are classed as "thermic" reactions.

The reaction between aluminium and calcium oxide (lime) has been specially studied by **Weston** and **Ellis**.[1] It only occurs when the ingredients are heated in a furnace, and is then by no means complete. It seems, therefore, to differ from the reactions between aluminium and other metallic oxides in being endothermic, and the authors conclude that calcium has greater affinity than aluminium for oxygen. They found that magnesia (magnesium oxide) was quite unattacked by aluminium. With alumina itself, aluminium yields a blackish grey product, probably containing a suboxide.

Aluminium will react with certain non-metallic oxides, *e.g.*, boron trioxide and silica. In the former case the product of the reaction contains aluminium boride and aluminium nitride (the nitrogen coming from the air) as well as alumina and free boron. In the latter case impure silicon is obtained as a crystalline body containing aluminium. Aluminium will also react with charcoal; in this reaction the air seems to play an important part, the product containing aluminium oxide and nitride, as well as aluminium carbide (Al_4C_3), together with unchanged aluminium and carbon.

Aluminium readily reacts with many metallic sulphides. In the reaction with lead sulphide already mentioned, if finely powdered aluminium is used, sufficient heat may be generated to volatilise the lead and produce explosion. **Goldschmidt**, at the time of the announcement of his discovery, had also succeeded in reducing sulphides of the following metals by means of aluminium—iron, cobalt, nickel, molybdenum and zinc.

---

[1] During the 1939–45 war both calcium and magnesium were obtained on a commercial scale by reducing the oxide with aluminium, *in vacuo*, at 1,200° C. For further details see p. [illegible]

Aluminium will also reduce phosphates, sulphates, and nitrates, the reactions with sulphates being more violent than those with nitrates.

Weston and **Ellis** have succeeded in bringing about the reaction between aluminium and sodium peroxide and aluminium and ferric oxide *in vacuo*, using an electrically heated iron wire to start the first reaction, and employing this reaction to initiate the second.[1]

Similar reactions in which bodies other than aluminium are employed are also known. For instance, **F. M. Perkin** has found that a mixture of calcium hydride (CaH_2) and cupric oxide in the proportion of two molecules of the latter to one of the former can be readily ignited with the production of copper, lime, and steam, the temperature, however, being insufficient to melt the whole of the copper produced. A mixture of antimony sulphide with calcium hydride is also very easy to ignite, the mixture swelling up as the reaction proceeds in a manner resembling that in which mercury thiocyanate (Pharaoh's serpents) behaves when ignited.[2]

Goldschmidt has succeeded in bringing about the reduction of metallic oxides, etc., by means of metallic calcium. He has found that whilst this metal reacts with oxides in a very violent manner, no regulus of metal is produced because of the limited fusibility of the calcium oxide formed. He has found, further, that, whereas negative results are obtained if silicon is substituted for calcium, a mixture of calcium and silicon will react satisfactorily with metallic oxides, giving a fusible slag of calcium silicate.[3]

G. F. Jaubert has patented mixtures which, on ignition, react "thermically" with the evolution of hydrogen.[4]

TECHNOLOGICAL PREPARATION OF METALS AND ALLOYS BY THE "GOLDSCHMIDT REACTION"

The preparation of metals and alloys by the Goldschmidt reaction is, as already mentioned, an exceedingly simple matter. All that is necessary is to make an intimate mixture of the oxide or mixture of oxides (in the right proportion) with slightly less than the theoretical weight of aluminium powder. The mixture must be dry, and is preferably heated before starting the reaction, which is done by means of a fuse, as already described. After the reaction has ceased, the metal or alloy will be found at the bottom of the crucible in which it is carried out. One great advantage of the method is that products can be obtained free from carbon. In the case of chromium and manganese, it is found that the low oxides give rather poor yields, whilst the high oxides act explosively. **Goldschmidt** and **Weil** find that the yield can be much improved, without the reaction becoming explosive, if the lower oxides are used with the addition of a small amount of the higher oxides.

The following are some of the metals and alloys actually manufactured by this method, and on the market at present.

(A) Metals.[5]

(1) **Chromium.**—"Thermic" chromium has a purity of about 98–99 per cent.; the impurities consist of iron and silicon. It is a brittle metal, of melting point higher than that of platinum, but alloying easily with liquid steel. It is employed in the manufacture of steels with a high chromium content, mainly crucible-steel for the best grades of high-speed tool steel. It is also used in ordnance manufacture.

---

[1] F. E. Weston and H. R. Ellis.—"Thermic Reactions in Vacuo," *Transactions of the Faraday Society*, Vol. VI., pp. 144 *et seq.* (1910.)

[2] F. M. Perkin and L. Pratt.—"Reducing Action of Metallic Calcium and Calcium Hydride upon Metallic Oxides, Sulphides, and Halogen Salts," *Transactions of the Faraday Society*, Vol. III., pp. 179 *et seq.* (1907).

[3] English Patent, No. 788 (1906).

[4] English Patent, No. 153 (1911).—"Hydrogen" in "Industrial Gases" (Crosby Lockwood, 1910).

[5] T. Burchell.—"The Aluminothermic Process," *J. Inst. Min. and Met.*, July 1949. See also p. 76.

(2) **Molybdenum.**—"Thermic" molybdenum has a purity of about 98-99 per cent., the impurities being similar to those in the case of chromium. It is used for rendering steel specially hard, and thus finds an application in the manufacture of tool steels. In this property it is said to be preferable to tungsten. "Thermic" molybdenum, being in fused lumps, does not oxidise in the air like the ordinary powdered variety.

(3) **Manganese.**—"Thermic" manganese has a purity of 96-97 per cent. The chief impurities are iron and silicon. It is very brittle, and fuses at a lower temperature (*circa* 1,227° C.) than chromium. It is used in the manufacture of very hard steel (12-14 per cent. Mn), which may be subjected to considerable strain, and also to alloy with other metals and alloys. It may be added in any amount to zinc-copper alloys, whose strength and other properties are thereby improved. It may, to about 2 per cent., be added to nickel castings to act as a deoxidising agent, whereby the density is increased, for which purpose its use does not occasion the deleterious effects sometimes produced by magnesium. A very small proportion of manganese is found to improve the colour of German silver, and is used with advantage as a deoxidising agent in the case of many other alloys, though it should not be employed with copper-tin alloys containing more than a very low percentage of tin.

(B) Alloys.

(1) **Chromium-Molybdenum,** 50 per cent. Cr, 50 per cent. Mo.

(2) **Chromium-Manganese,** 30 per cent. Cr, 70 per cent. Mn.

(3) **Chromium-Nickel,** 10 per cent. Cr, 90 per cent. Ni, and 50 per cent. Cr, 50 per cent. Ni.

(4) **Chromium-Copper,** 10 per cent. Cr.

The alloys of chromium with molybdenum, manganese, and nickel are used in the manufacture of hard steels. Those with manganese and copper may be added with advantage to copper, and increase its elasticity.

(5) **Molybdenum-Nickel,** 75 per cent. Mo, 25 per cent. Ni.

(6) **Ferro-Molybdenum,** 80 per cent. Mo.

Ferro-molybdenum may be used in place of molybdenum in the manufacture of hard steel, and the price of the alloy is less per weight of molybdenum it contains than that of the pure metal. The molybdenum-nickel alloy is used in the manufacture of saws.

(7) **Ferro-Titanium,** 23-25 per cent. Ti, 70-72 per cent. Fe, 5 per cent. Al.

This alloy is extensively used as a cleansing agent for all classes of steel. The presence of the small proportion of aluminium renders the alloy more soluble; moreover, the aluminium acts as a deoxidising agent, leaving the titanium free to remove nitrogen, and further, it produces a slag of aluminium titanate, which is more easily fusible than either alumina or titanic oxide. Steel treated with this alloy is rendered tougher and denser.

(8) **Ferro-Vanadium,** 35 per cent. Va, 1-2 per cent. impurity (Al and Si).

Added to mild steel, vanadium in slight amount considerably increases its elasticity. It may also be added to iron castings to render them tougher.

(9) **Ferro-Boron,** 20-25 per cent. Bo.

This alloy added to steel acts in a somewhat similar way to carbon, but it is only infrequently employed.

(10) **Manganese-Copper** (iron-free), 30 per cent. Mn.

(11) **Manganese-Tin** (lead-free), 50 per cent. Mn.

(12) **Manganese-Zinc** (lead-free), 20 per cent. Mn.

(13) **Manganese-Titanium,** 30-35 per cent. Ti.

These manganese alloys are used in place of pure manganese in the manufacture of non-ferrous alloys. In the preparation of those containing tin and zinc, the slag formed on the molten tin and zinc must be removed before adding the manganese, and the charge kept heated for several hours. Manganese titanium alloy is used for removing oxygen and nitrogen from copper alloys.

(14) **Ferro-Columbium,** 60-66 per cent. niobium, 5.5-6.5 per cent. tantalum.[1]

In this connection may be mentioned the use of titanium "thermit" in foundry work. This preparation consists of ordinary "thermit" containing a small proportion of titanium oxide, and is put up in tins, through which are drilled a couple of holes, by means of which the tin can be fastened to a rod. As soon as the molten metal is run from the furnace into the ladle, the tin of titanium "thermit" is plunged in and held at the bottom until the reaction is over. The slag rises to the top, and can thus be easily removed. The effect of the treatment is to cleanse the metal from impurities, thus increasing its fluidity, and producing a finer and closer grain; moreover, the sulphur content is reduced.

---

[1] See paper by T. Burchell, *loc cit.*

USES OF "THERMIT" AS A HEATING AGENT

The uses of "thermit" as a heating agent are defined by the nature of the "thermit" fire. As **Goldschmidt** has pointed out, "thermit" provides us with a fire differing in certain important respects from all other fires. In the first place, in the combustion of "thermit," neither is air consumed nor is any gas evolved, as in the case of the combustion of wood, coal, coal-gas, producer-gas, or petrol. The most important difference, however, is in the heat-density. The actual amount of heat obtainable from a given weight of "thermit" is considerably less than that obtainable from the same weight of anthracite;[1] but in the former case the whole of this heat is, so to speak, obtained at once, since the reaction between aluminium and iron oxide takes a very small period of time from commencement to completion, even when the weight of material is very considerable. Indeed, in the combustion of "thermit," a heat-density is produced not otherwise obtainable, the actual temperature being considerably above that of the electric furnace. Where a continuous heating effect rather than density of heat is the essential desideratum, "thermit" would be useless; thus it is not suitable for locomotive purposes, or for cooking generally.[2] But where great density of heat is required, "thermit" is preferable to other sources of heat, because by its aid one can so readily produce an enormous temperature at a moment's notice.

The chief uses of "thermit" as a source of heat are in the butt-welding of pipes, and for reheating sluggish metal in foundry practice.

For the latter purpose the "thermit" is made up in tins, which are employed, when it is desired to reheat the metal in the ladle, in a similar manner to that used in the case of titanium "thermit." Tins of "thermit" may also be placed in the risers of castings, and are found particularly useful in making intricate castings, or those that are long and narrow (*e.g.*, ships' stems and stern posts). In such cases the tins should be built into the moulds. A pinch of ignition powder is necessary to initiate the reaction in the case of cast iron, but is not required in the case of steel.

The butt-welding of iron or steel pipes is accomplished in the following manner:—The ends of the pipes to be welded together are surrounded by a suitable mould, into which the products of the "thermit" reaction are poured. Welding temperature being reached, the ends of the pipes are pressed together by means of screws placed in position beforehand. For pipes not exceeding ¼ in. in thickness, special cast-iron moulds with handles have been designed, and can be used over and over again; but for larger pipes it is advisable to use sheet-iron moulds (made in the shape of a horseshoe, in two pieces) banked round with damp (but not wet) sand. Of course, if the liquid iron, formed by the reaction, were allowed to come into contact with the pipes they would be fused through, but it is found that the alumina slag, which first issues from the crucible when the products of the "thermit" reaction are poured out, solidifies on the surfaces of the pipes, thus forming a highly refractory protective coating, through which the metal cannot penetrate.

During the world wars a deplorable application for the "thermit" fire has been found in the construction of incendiary bombs—unfortunately, so many scientific discoveries, which rightly applied are of the greatest utility to man, may be debased to vile ends. For further details see page 75.

The "thermit" fire is peculiarly adapted for purposes of destruction, inasmuch as it is so difficult to extinguish. Fire may usually be extinguished (i.) either by cutting off the supply of oxygen (air) necessary to the combustion of the burning body, by means, for example, of blankets, sand, carbon dioxide, etc., or (ii.) by wetting the body with a non-inflammable liquid (*e.g.*, water), which not only to some extent screens it from the air, but, by extracting much of its heat, reduces its temperature below that at which the combustion will take place. In the case of the "thermit" fire, however, like that of gunpowder and similar mixtures, no external oxygen is needed for the combustion, hence screening it from the air is without effect, as is evident from the equation representing the reaction, and is demonstrated by the experiments of Weston and Ellis mentioned above. Moreover, the temperature is sufficiently high to decompose water, with the evolution of hydrogen, which itself is highly inflammable—

$$3Fe + 4H_2O = F_3O_4 + 4H_2.$$

---

[1] Goldschmidt gives the following figures: 1 kilogram of "thermit" gives 450 cals., 1 kilogram of anthracite gives 7,000 cals.

[2] As concerns cooking, it may be mentioned that the "Deutsche Munitions und Waffenfabrik," of Karlsruhe, have constructed a cooking and roasting stove for camp cooking.

On the other hand, of course, the burning of objects set fire to by the "thermit" fire may be extinguished in any way ordinarily applicable.

The "thermit" incendiary bombs used by the Germans in the first world war were usually conical in shape, with a flat metallic cup, about 10 ins. in diameter, as base. On this is fitted a pierced metallic funnel filled with thermite, with a metallic cap and handle at the top. Generally some yellow phosphorus, which is not only highly inflammable, but generates nauseous fumes on combustion, is introduced at the base of the funnel. Outside the funnel is a padding of highly inflammable resinous material, which is bound on with rope, wires being fastened from the outer rim of the cap to that of the base to increase the stability of the bomb. The rope used is probably first treated so as to increase its inflammability. Occasionally celluloid chippings are added, and more rarely a small amount of petrol.

USES OF "THERMIT" AS A HEATING AGENT AND SOURCE OF MOLTEN STEEL

Not only may the heat derived from the "thermit" reaction be utilised in welding, but the liquid steel produced at the same time may be employed to form a bulb around the joint, thereby greatly strengthening it. This method of welding, patented by **Goldschmidt**, has been very extensively employed in the welding of tram-lines.

The rails which are to be welded by this method should have no bolt holes, and the ends should be undercut $\frac{1}{16}$ in. in order to ensure a proper butt-weld. They must be brought into true alignment and clamped tightly together. The "thermit" is ignited in a crucible with a hole in the bottom fitted with a device for tapping. Moulds of sand of a loamy and plastic nature, mixed with quartz of not too close-grained or clayey a character, but as free, porous, and sharp as will permit of binding, are constructed so that the "thermit" steel, which first issues from the crucible when it is tapped after the reaction is over, runs to the bottom of the rail, forming a metal bulb over the joint to about half-way up the rail or more. The moulds must be thoroughly baked, coated with graphite, and the two sections carefully luted together. It is very essential that everything with which the products of the "thermit" reaction come into contact should be thoroughly dry and warm. The molten metal, of course, must not be allowed to come in contact with the top of the rail, which should be completely covered by the molten alumina which issues from the crucible after the metal has flowed out. When welding temperature has been reached the rails are pressed together by means of clamps placed in position beforehand.

Third, or conducter, rails may also be similarly welded, or conduction may be ensured simply by welding a small bridge of "thermit" metal on to the base of the rail.

In the case of rails containing high percentage of carbon a modified method of welding, known as the "Stelcop" (Steel-Copper) process, is employed. The main point in this process is that prior to welding, and after the rails have been placed in alignment, a thin copper-coated steel shim is introduced between the rail heads. The rail ends are, for welding by this process, not undercut, and the clamps are not screwed up after welding. The heat of the molten slag surrounding the rail heads melts out the copper and leaves them firmly welded together.

Tests carried out on rails welded by means of "thermit" have proved eminently satisfactory. The following are typical results:—

BENDING TESTS

Description.	Span.	Loads. Elastic Limit.	Bending Moment.
Solid rail - - - - - - -	10 ft.	28,200	70,500
Fishplate jointed rail - - - - -	10 ,,	10,000	25,000
"Thermit" jointed rail - - -	10 ,,	25,000	62,500
Solid rail - - - - - - -	5 ,,	74,000	92,500
"Thermit" jointed rail - - -	6 ,,	42,000	63,000

CHEMICAL TESTS

Ordinary Steel Rail.		"Thermit" Weld.		Drillings from Rail Head near Welded Joint.		Drillings from Rail Head away from Welded Joint.	
Iron	98.520	Iron	97.82	Iron	98.3743	Iron	93.331
Manganese	0.865	Manganese	trace	Manganese	1.009	Manganese	1.038
Phosphorus	0.042	Phosphorus	,,	Phosphorus	0.067	Phosphorus	0.065
Sulphur	0.054	Sulphur	0.02	Sulphur	0.059	Sulphur	0.058
Silicon	0.021	Silicon and Insoluble	0.51	Silicon	0.0027	Silicon	0.018
Carbon	0.498	Carbon	0.11	Carbon	0.488	Carbon	0.490
Arsenic	trace	Aluminium	1.48	These analyses indicate no alteration in the composition of the steel in the rail head.			

HARDNESS TESTS[1]

Load on Die in Tons.	Welded Rail. Length of Indentation Produced.	
	Away from Joint.	Close to Joint.
0.25	0.26 in.	0.26 in.
0.50	0.32 ,,	0.32 ,,
0.75	0.37 ,,	0.36 ,,

Metal tested from head of rail.

It is clear from the results of the hardness test that the subjection of the welded edges of the rail to the high temperature of the reaction had no injurious effect on the hardness of the rail.

The liquid steel produced by the "thermit" reaction may also be used in repair work of every character, not only in the case of small articles, but in that of the very largest. Indeed, by the ignition of a couple of hundredweights of "thermit," one may produce in a few moments a hundredweight of superheated mild steel; a quantity producible in so short a period of time by no other means. Crucibles, similar to those employed in the welding of tram-lines, are employed, the details of the method depending, of course, on the type of repair to be effected. The process has been sanctioned by the British Corporation for the Survey and Registry of Shipping for repairs to fractured stern posts, rudder frames, and damages of a similar character. The results of the Corporation's bending tests (July 1909) on "thermit" welded bars are here appended, and show that the welded bars were considerably stronger than an unwelded bar.

---

[1] The relative hardness was determined by measuring the lengths of indentations made by a hardened steel die with a curved edge struck to a radius of 1 in., and having a cutting edge whose angle was 50°.

Description.		Distance between Supports.	Load Applied in Tons at Centre of 3-ft. Supports.																Maximum Stress. Tons.	Remarks.
			Deflection and Set in Inches.																	
Mark.			Load in Tons.	5	20	30	35	40	50	60	70	80	90	100	110	120	130	140		
K1	5 in. square "thermit" welded bar	3 ft.	Defln.	zero	...	.02	.06	.08	.10	.12	.40	.80	.85	1.02	1.38	1.85	2.58	3.72	143.0	The bar broke outside the weld. Fracture, finely granular.
			Set	...	...	...	...	...	.02	.00	...	...	...	...	...	...	...	...		
K2	5 in. square "thermit" welded bar	3 ft.	Defln.	zero	.02	.06	.08	.09	.11	.13	.20	...	...	...	...	...	...	...	71.5	Bar deflected 0.30 in. Load applied, half maximum applied to bar K1. No sign of cracking.
			Set	...	...	...	none	.05	.06	.07	...	...	...	...	...	...	...	...		
K3	5 in. square unwelded bar	3 ft.	Defln.	zero	...	none	.02	.05	.10	.38	.75	1.20	1.88	2.00	4.62	6.33	...	...	123.15	The bar continued to bend without any further increase of load, and the test was stopped after bending through an angle of 50°. No sign of cracking.
			Set	...	...	...	...	...	.03	.30	...	...	...	...	...	...	...	...		
K4	5 in. square "thermit" welded bar	3 ft.	Defln.	zero	...	.02	.04	.08	.08	.10	.22	.48	.70	1.08	1.50	2.25	3.18	...	139.60	The bar broke outside weld. *FRACTURE:* Finely granular.
			Set	...	...	..	...	none	.03	.05	...	...	...	...	...	...	...	...		

In repair work it is frequently found advantageous to add a certain proportion of steel punchings to the "thermit"; this reduces the weight of "thermit" required (and hence the cost) and renders the action less violent. As to the chemical composition of the steel obtained from "thermit," the following figures are typical of modern practice:—

Carbon	0.2	per cent. to	0.3	per cent.
Manganese	0.5	,,	0.6	,,
Silicon	0.25	,,	0.5	,,
Sulphur	0.03	,,	0.04	,,
Phosphorus	0.03	,,	0.04	,,
Aluminium	0.07	,,	0.18	,,

The figures of the Manchester Corporation Tramways for the weld in tram-rails, which differ slightly from these, have already been given.

USES OF "THERMIT" SLAG

In the slag from the reaction of chromium "thermit," minute red-coloured crystals are found, which must be regarded as rubies, the ruby consisting of nothing but alumina coloured by chromium. They are too small to be of any commercial value.

Important commercial uses have, however, been found for the alumina which constitutes the slag formed in the reaction between aluminium and metallic oxides. The alumina thus obtained has been given the registered name "corubin." Owing to its comparative freedom from other metallic oxides and absolutely anhydrous condition, it is harder that natural emery and is therefore found to be preferable to it for polishing purposes. Moreover, according to **Dr Buchner** of Mannheim, it is preferable to natural corundum (which it resembles) in the manufacture of pottery, for which purpose it is mixed with clay and burned. It is claimed to be especially useful for making chemical apparatus which may be subjected to great changes in temperature without fracturing.

Mode of Ignition of Thermit

The mixture is normally ignited by a "pill" of barium peroxide and aluminium powder, which is itself ignited by a fuse of magnesium ribbon. Electrical methods may, however, be used, as in the reference by K. Rose (*loc. cit.*), when thermit is used for demolition.

Modern Use of Thermit for Incendiary Bombs

For industry, the thermit mixture usually consists of 3 parts of powdered aluminium to 10 parts of magnetite (Fe_3O_4), but for military purposes the mixture usually consists of 24 per cent. aluminium with 76 per cent. of magnetite. The mixture is usually compressed at 12,000 lbs. per square inch, and sodium silicate may be added as a binder. In this case the mixture requires drying out thoroughly before use. Celluloid and sulphur have also been used as binders with good results.

The normal initiator, a mixture of barium peroxide and aluminium, is used where a scattering effect is not required, but where a scattering effect is required, a mixture of 9 parts of magnesium powder with 13 parts of potassium chlorate is used.

Other modified thermit bombs used during the two world wars contained copper, nickel, or manganese as oxides, magnesium metal, and barium nitrate.

The casings of incendiary bombs are usually made of a magnesium alloy containing about 7 per cent. of aluminium and a little manganese. The aluminium is used to improve casting properties and to lower the melting point. When the thermit mixture in the bomb ignites, the heat generated is sufficient to melt the casing and to cause the magnesium alloy to burn fiercely. The heat liberated by the thermit part of the incendiary bomb is 758,000 cals. per gram. mol. of aluminium.

Use of Thermit for Demolition

An interesting recent application of thermit is for the demolition of steel structures. An article by K. Rose (*Metals and Alloys*, **20,** No. 6, 1620, 1944) describes the felling of a bridge, at the South Chicago plant of the Interlaken Iron Corporation, 300 ft. long, 80 ft. high, and 30 ft. wide, in 51 seconds, by thermit, fired electrically from a distance so as to avoid danger to workmen.

Modern Developments in Welding and Fabrication by Thermit

A recent paper in *Welding* **17,** No. 3, 94, 1949) describes how large repairs are carried out, or prefabricated heavy steel parts welded together, by the thermit process. The method most favoured is that in which the molten steel, formed by carrying out the reaction in a conical crucible, is allowed to flow into the gap between the parts, which is surrounded by a refractory mould. In the case of a repair, the gap is first cleaned out by cutting with the oxyacetylene flame. The parts to be joined are heated to red heat before admission of the molten steel and the whole operation is carefully timed so as to ensure making a perfect joint. Cooling is normally for 24 hours before the joint is disturbed.

The thermit mixture consists essentially of finely divided (granulated) aluminium and specially prepared iron oxide. Minor ingredients are carbon and manganese, whilst molybdenum, nickel, vanadium, and chromium may also be added if desired. The reaction is represented by the equation—

$$8Al + 3Fe_3O_4 = 9Fe + 4Al_2O_3$$

The tensile strength of the steel produced is 29 t./sq. in. with a yield point of 20 t./sq. in.

Typical applications are the repair of mill housings, cylinders, ship frames, crank shafts, tractor and excavator components, and the construction of ship stern frames, or freight wagons. Continuous lengths of rail lines are now joined with thermit in the British Commonwealth and other countries, generally by the fusion process just described. For example, the Moffat Tunnel, 50 miles N.W. of Denver, Colorado, contains 66,000 ft. of continuously welded rail. Such applications of thermit are far more common in the U.S.A. than in England, and the process is much more useful for many purposes than is generally supposed in England. Metal and Thermit Corporation of New York are the leading exponents in the U.S.A., whilst the Evans Welding Company and Murex Limited operate such processes in England. Messrs Murex Limited acquired the business of Thermit Limited in 1929.

Modern Smelting Practice

A recent paper by T. Burchell ("Symposium on the Refining of Non-Ferrous Metals," *J. Inst. Min. Met.*, July 1949) describes the modern theory of the **aluminothermic processes** and, particularly, the smelting of manganese, chromium, and ferro-columbium. Production of these metals and alloys is said to be 1,100 tons per month in the Rainham works of Murex Ltd. by variants in the aluminothermic process. One interesting process described in this paper is that in which the thermit mixture is added continuously to the crucible as the reaction proceeds. In the ordinary method, a full crucible of thermit mixture produces only about one-third of a crucible of molten metal and slag, whereas by adding more mixture as the reaction proceeds, the full capacity is used, and several tons of product can be obtained in one operation.

Related Properties of Aluminium Powder

Aluminium powder is used as a deoxidant in a number of metallurgical operations. In the open hearth process for the manufacture of steel, the addition of aluminium powder reduces the ferrous oxide, which is the main cause of unsoundness. The amount added should only be sufficient to combine with the oxygen in the oxide, otherwise inclusions of aluminium will be present in the steel. The usual quantity used is 1–2 lbs. per ton of steel. The addition of aluminium to the ladle also has the effect of producing a fine grain structure in the steel. This effect is accentuated by the presence of silicon, so that certain ferro-silicon-aluminium alloys are sometimes added to the melt where close grained steel is required.

The pronounced reducing properties of aluminium powder are apparent from its behaviour with chemical oxidising agents. For example, aluminium powder when mixed with sodium peroxide and moistened will explode; when heated with powdered potassium permanganate the powder burns with great rapidity; whilst heated aluminium powder will also combine with gaseous chlorine and nitrogen.

Ammonal is a powerful explosive mixture of aluminium powder and ammonium nitrate. It is usually modified before use as an explosive, and a typical composition of modified ammonal, according to Bally, is—

30–75	per cent. of	ammonium nitrate.
10–25	,,	aluminium powder.
12–40	,,	T.N.T.
0–3	,,	carbon.

The Production of Powdered Aluminium

The processes normally used for producing aluminium powder are known as milling, shotting, granulation, and atomisation. Milling produces aluminium in flake form, suitable for use as a pigment, whilst the others produce powder suitable for aluminothermics. Atomisation, in which a stream of molten metal is disintegrated by a blast of compressed fluid, is the most versatile process, and produces a wide variety of powders suitable for the various processes related to the thermit process. A detailed discussion of the process variables in the production of aluminium powder by atomisation has recently been published by J. S. Thompson. The normal process used is similar to that of a metal spray gun, using compressed air as the fluid medium.

Production of Metallic Calcium and Magnesium by Reduction with Aluminium

The reduction of calcium oxide by aluminium takes place readily at a temperature of 1,200° C. (*cf.* C. C. Loomis, Electrochemical Society Report, 89th General Meeting, Birmingham, Ala., April 1946), according to the equation—

$$6CaO + 2Al = 3Ca + 3CaO.Al_2O_3$$

In the wartime plant erected by the New England Lime Co. at Caneen, Connecticut, for the production of calcium for the U.S. Signal Corps, metallic aluminium, ground or granulated to pass through a 20-mesh sieve, was made into briquettes with high purity, high calcium, limestone, in approximately equal proportions, using ovoid presses, without the use of a binder. The briquettes were coked in small ovens, *in vacuo*, when the reduced calcium distilled off and collected in the 10-in. diameter steel exit pipe leading from the retorts. The walls of the retorts, 1.1in. thick, were made of 28 per cent. Cr, 15 per cent. Ni alloy, the dimensions of the oven were 10 ins. wide by 10 ft. long. At the high operating temperature the walls slowly collapsed, but the ovens were blown into shape again by air pressure (100 lbs./sq. in.) when necessary. The cooled ingots of calcium could be extruded or rolled into sheets. Peak production was 10,000 lbs. of calcium per day. Magnesium was also produced in a similar manner.

SECTION LIX

THE CALCAREOUS CEMENTS INDUSTRY

By Ernest A. Dancaster, B.Sc. (Lond.)
Revised by Wilfrid Francis

LITERATURE

E. A. Dancaster.—"Limes and Cements." London, 1920.
E. C. Eckel.—"Cements, Limes and Plastics." London, 1928.
F. B. Gatehouse.—"Handbook for Cement Works Chemists." London, 1928.
G. Martin.—"Chemical Engineering and Thermodynamics applied to the Cement Rotary Kiln." London, 1932.
A. B. Searle.—"Limestone and its Properties." London, 1935.
F. M. Lea and C. H. Desch.—"Chemistry of Cement and Concrete." London, 1935.
L. C. Urquhart and C. E. O'Rouke.—"Design of Concrete Structures." 1940.
S. Baker and A. DeGroot.—"Cements and Concrete." Scranton, Pa., 1941.
R. H. Boque.—"The Chemistry of Portland Cement." New York, 1947.
Cement and Concrete Association.—"Cement in the Making." London, 1947.
—— "Bibliography of Cement and Concrete." London, 1949.
A. C. Davis.—"Portland Cement." London, 1948.
Lafarge Aluminous Cement Co.—"Refractory Cement." London, 1949.
W. Watson and Q. L. Craddock.—"Cement Chemist's and Work Manager's Yearbook." London, 1940.
J. C. Witt.—"Portland Cement Technology." New York, 1947.
N. D. Green.—"Concrete for the Contractor." London, 1947.
F.I.A.T. 519.—"German Cement Industry." 1946.
F.I.A.T. 1123.—"Precast Concrete Products Industry in Germany." 1948.
B.I.O.S. 1663.—"The Use in Germany of Waterproofing and other additions to Mortar and Concrete." 1948.

The following *British Standard Specifications* are important:—

No. 12. Ordinary and Rapid Hardening Portland Cement.
No. 146. Blast Furnace Portland Cement.
No. 1370. Low Heat Portland Cement.
No. 915. High Alumina Portland Cement.
No. PD 572. Machine for Testing Portland Cement.
No. 890. Building Limes.

There are 26 Standard Specifications relating to *concrete* and articles made of concrete.

The following *A.S.T.M. Specifications* are important:—

C. 150–47. Portland Cement.
C. 175–47T. Air Entraining Portland Cement.
C. 205–47T. Blast Furnace Slag Cement.
C. 10–37. Natural Cement.
C. 91–40. Masonry Cement.
C. 91–44T. Masonry Cement (Tentative).

Also see *A.S.T.M.* Standards on Cement, 1942 Edition.

The calcareous cements are compounds of calcium. They are divided into limes and cements according to their composition and behaviour towards water, but the division is only a matter of convenience, because they are all cements. The **limes** consist of more or less pure calcium oxide, CaO, and the **cements** consist of salts, such as silicates and aluminates. Limes "slake" or crumble to powder, with more or less evolution of heat, when treated with a little water, the action being very energetic in the case of pure lime, and very slow in the case of hydraulic limes. Cements, on the other hand, do not slake when in contact with water, but "set" or solidify without any perceptible change of volume, and with little evolution of heat. The hydraulic limes also possess the property of setting under water, but are distinguished from the cements by their power of slaking. The whole group of calcareous cements may be classified as follows:—

LIMES.
Common lime.
Hydraulic limes.
Hydrated limes.

CEMENTS.
Puzzuolanic and slag cements.
Natural cements.
Portland cement.
Plaster cements.
Ciment fondu.

This classification, however, can only be considered as approximate, because some of the classes merge into one another by imperceptible degrees. Thus, there are limes of every degree of hydraulicity between pure common lime and the true hydraulic limes, and the latter gradually pass into the puzzuolanic cements. Again, there is no hard and fast line between Portland cement and the natural cements, some of the latter being known as **natural Portland cements**, on account of their similarity to the artificial product.

COMMON LIME

The chemical properties of common lime, CaO, are discussed under **Calcium Salts,** Vol. I., p. 341. We here deal solely with its manufacture and its use as regards the cement and mortar industry. The lime is obtained by calcining calcium carbonate, $CaCO_3$, at a red heat, so as to drive off the water, which is generally present, and to expel the carbon dioxide, CO_2. The reaction takes place according to the equation—

$$CaCO_3 = CaO + CO_2.$$

The calcium oxide thus obtained is known as **quicklime, caustic lime,** or **common lime.** On adding a little more than the correct amount of water (18 parts by weight of water to 56 parts by weight of pure calcium oxide) chemical combination takes place. Owing to the heat of the reaction some of the water is expelled as steam, and the lime crumbles to a perfectly dry powder known as **slaked lime,** which consists of calcium hydrate, $Ca(OH)_2$—

$$CaO + H_2O = Ca(OH)_2.$$

For the **chemical properties** of slaked lime, see under **Calcium Salts,** Vol. I., p. 341.

Calcium carbonate occurs naturally in a number of forms, some of the best known being **marble, limestone,** and **chalk,** any of which will yield the oxide on calcination. For the **chemical properties** of calcium carbonate, see under **Calcium Salts,** Vol. I., p. 341.

Marble.—White marble consists of nearly pure calcium carbonate, and therefore yields a very pure lime. It is, however, too expensive to be used for the preparation of lime for ordinary purposes, and the lime produced is too rich to be used for building purposes, unless it be mixed with burnt clayey matter.

Limestone.—This is a very abundant, dense form of calcium carbonate, which is less pure than marble, and is sometimes very impure. It usually contains free silica, aluminium silicate, and magnesium carbonate. When the stone contains 5 per cent. or more of the last mentioned constituent it is known as **dolomitic limestone**, and when the amount reaches 23 per cent. it is known as **dolomite** or **magnesium limestone**: as limes containing much magnesia, MgO, slake very imperfectly, dolomites are not used for the manufacture of lime except for special purposes, as for the linings of some furnaces. Those limes which contain much aluminium silicate are used for the manufacture of hydraulic limes (which see, p. 82).

Chalk.—This is very similar to limestone, and varies in purity in the same manner. It is, however, much softer, and contains a considerable amount of water when quarried. The upper, or white, chalk yields a pure lime, whilst the lower, or grey, chalk yields a more or less hydraulic lime.

Other Sources of Lime.—Amongst other materials **sea shells** are used as a source of lime. The waste shells from the oyster canning industry are thus utilised at Baltimore and other places in America, and also in Holland. The lime obtained from this source is too rich to be used for building purposes unless it be mixed with puzzuolanic matter (see p. 83). A considerable amount of lime is obtained in India from deposits of impure calcium carbonate, known as **kunkur** or **kankar**, which is found in the alluvial soil of the plains. After burning, it is mixed with sand and water, and generally with a little molasses to form the rendering known in India as **chunam**. The only effect of the molasses is apparently to retard the drying, which might otherwise become too rapid in a hot climate.

Lime Burning.—The raw material is calcined in kilns at a temperature of not less than 812° C. (For dissociative pressures of $CaCO_3$ see Vol. I., under **Calcium Salts.**)

The operation is a simple one, as the burner has only to expel the water and carbon dioxide, and there are therefore no complicated reactions involved. It is, however, necessary to remove the products of decomposition, because calcium carbonate can be fused without decomposition in an atmosphere of carbon dioxide, yielding a marble-like mass. The removal of the carbon dioxide is effected by means of the natural draught of the kiln. The decomposition is facilitated in an atmosphere of steam, as was first shown by Gay Lussac, and it is a common practice to inject water or steam into the kilns for this purpose. Where this is not done, the lime burners often wet the material before burning, and thus obtain a certain amount of steam. The carbon dioxide produced during lime burning is usually wasted, although it is a valuable by-product. It is, however, sometimes utilised in condensing plants in Germany and the United States. See under **CO_2 Industry.**

Lime burning is a very ancient industry, the earliest form of kiln being probably a hole in the ground in which the mixed raw material and fuel were placed and ignited, the process being an intermittent one. Many forms of kiln for lime burning are in use at the present time, but they may all be classified under two heads: (1) **intermittent kilns**, in which the calcined charge is withdrawn when it is cold and the kiln restarted with a fresh charge, and (2) **continuous** or **draw kilns**, in which the raw material is fed in at the top and the lime is removed at the bottom, so that the process is continuous. Continuous kilns are subdivided into two classes, **stationary** or **vertical kilns**, and **rotary kilns**. The stationary continuous kilns may be of the mixed feed (**running**) or of the separate feed type.

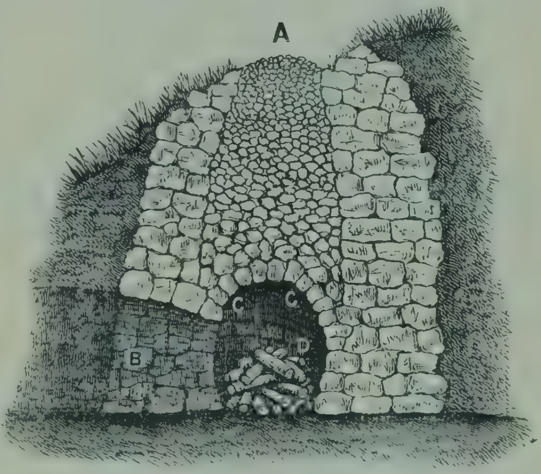


FIG. 1.—Intermittent Kiln.

The **flare kiln**, which is shown in Fig. 1, is a kiln of the first class. It is roughly egg-shaped, and, with the exception of a space at the bottom, is filled with lumps of limestone or chalk, supported on a roughly built arch of bigger lumps of the same material. The fuel is burnt on fire-bars in the space at the bottom of the kiln, and the hot gases ascending through the mass of limestone convert it into quicklime. The kiln has to be emptied and recharged for each batch, so that the process is intermittent. The lime thus produced is known as **flare lime.**

In its simplest form the kiln is built of the limestone itself, but kilns of this type are often constructed of brick or stone work, the inside being generally lined with fire-bricks set in fire-clay. These kilns are usually either cylindrical, with a truncated conical chimney, or they consist of two truncated cones placed base to base. The height of the kiln should be twice the largest diameter.

The raw material may be supported upon an iron grating, as in the **Deplinne & Donop's kiln,** and in some of the modern forms of this kiln producer-gas is used as fuel, in which case it is usual to employ an annular kiln, the raw material being placed in the central space so that it may attain a fairly high temperature before being charged into the surrounding kiln.

A modern form of continuous running kiln consists of a cylindrical or conical shaft with side openings a the bottom. The raw material and fuel are charged in at the top, and the lime and ash removed through the openings at the bottom. The shaft is often more or less egg-shaped. These are termed **mixed feed** kilns.

The process is continuous, fresh supplies of raw material and fuel being added at the top as the charge sinks, and the lime and ash being removed as they are formed. Other kilns of this type are the **Dietzsch kiln** (see p. 111), and a modified form of the **Aalborg** or **Schofer kiln** (see p. 112).

In vertical kilns with **separate feed,** the stone enters at the top and the fuel through the sides (*e.g.*, the Spencer and Keystone Kiln). The fuel may be (*a*) solid, *i.e.*, coke, coal, or anthracite, or (*b*) gas—usually producer gas.

In some kilns (*e.g.*, the Brockham Kiln) a portion of the solid fuel enters at the top with the stone, but the greater part enters through the sides.

The **Keystone lime-kiln** shown consists of a steel cylinder lined with fire-brick and resting on a heavy steel base. Beneath the cylinder is an inverted, truncated steel cone called the **cooling** cone. The furnaces are carried on steel platforms which extend beyond the firing doors in order to give sufficient room for working. The cylinder is charged with the raw material and the flames from the furnaces are directed on to the stone through two large openings lined with fire brick in the walls. After passing through the burning zone the lime falls into the cooling cone, from which it is withdrawn by means of draw-gates in the bottom. The heated air around the cooling cone passes into the ashpit under the grates, thus adding to the efficiency of the furnace, and sometimes a steam jet is placed in the hot air passage in order to provide forced draught. The **Rudersdorf kiln** shown in section in Fig. 2 is a well known kiln of this class. It is polygonal in plan and consists of a central shaft about 40 ft. high, to which the fire chambers are connected by means of arched openings. This central shaft is about 10 ft. in diameter at the widest part, just above the fire chambers, and tapers off above and below; at the top, where the raw material is added, it has a diameter of about 7 ft. Many modifications of this kiln are in use, **Rumford's kiln** being one of the best known. In the Fahnehgeln Kiln (Fig. 3), the Schmatolla Kiln (Fig. 4) and the Priest Kiln producer gas is made near to the kiln and is used to burn the stone. Gas firing produces purer lime of more uniform composition than solid fuel.

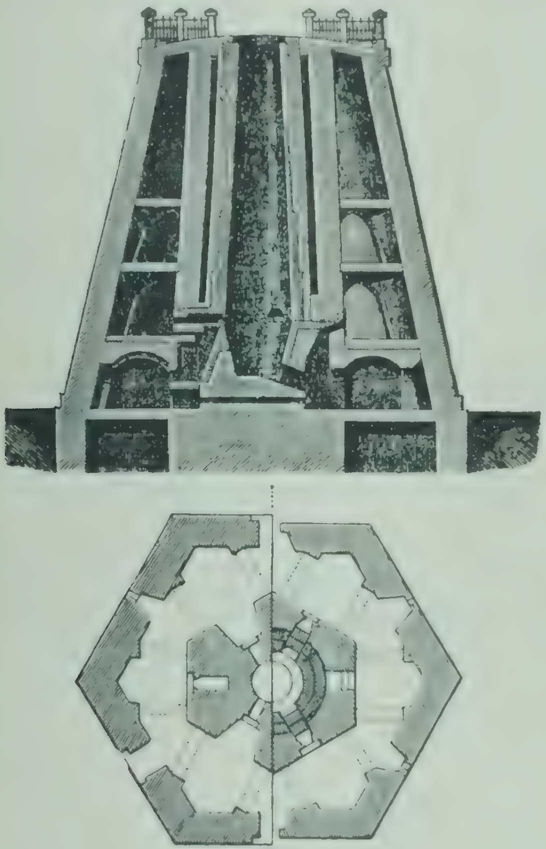


FIG. 2.—Rüdersdorf Kiln.

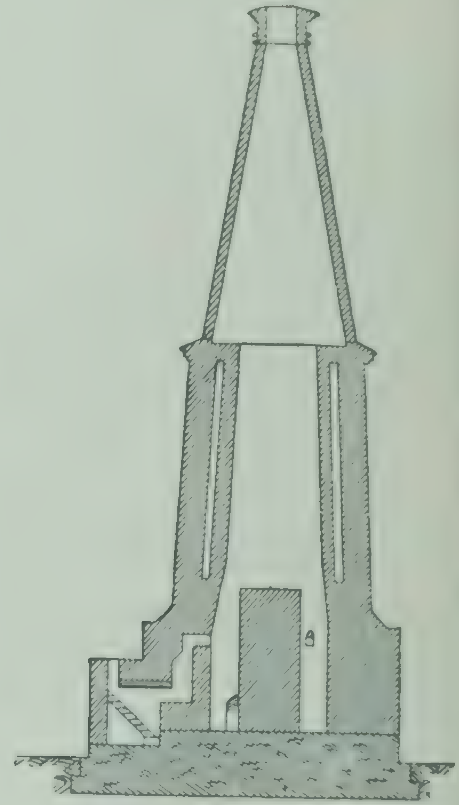


FIG. 3.—Fahnehgelm Kiln.

The **Hoffman ring kiln** (see pp. 231 *et seq.*) may be regarded as forming a connecting link between the intermittent and continuous types of kilns; because although it is continuous as a whole, each of the chambers into which it is divided acts as an intermittent kiln.

Rotary kilns similar to those used for the manufacture of Portland cement (see p. 100), but worked at a lower temperature, are also employed for burning lime. They cannot be used where the lime is required to be in large lumps.

HYDRATED LIME

Lime which has been slaked under carefully controlled conditions is known as hydrated lime. It is in the form of a fine white powder and when properly made it is fully slaked and free from quick lime. In a **hydrator**, the lime—preferably crushed to small pieces—is mixed mechanically with a suitable proportion of water. Too little water will produce an unsound hydrate and too much will form a damp adhesive mass. The lime stays in the hydrator sufficiently long to ensure complete admixture of the lime and water, and then passes into an air-separator or cyclone in which the coarse particles are separated. The fine particles are then packed in paper bags.

Hydrators are of two types:—

(*a*) **Batch hydrators** consisting of a large closed pan in which a weighed charge of lime and a suitable quantity of water are mixed by rotating paddles or scrapers.

(*b*) **Continuous hydrators,** which are usually cylindrical in shape, through which the mixture of lime and water is passed by means of a rotating screw.

Various devices are used to prevent the escape of lime dust and to control the process of hydration.

British Standard Specification No. 890 specifies the properties of good commercial hydrated lime.

Relatively pure limes, which slake rapidly with a considerable evolution of heat, and yield a large volume of powder, are called **fat** or **rich** limes, whilst those which slake slowly and with little evolution of heat, yielding a comparatively small volume of powder, are called **lean** or **poor** limes.

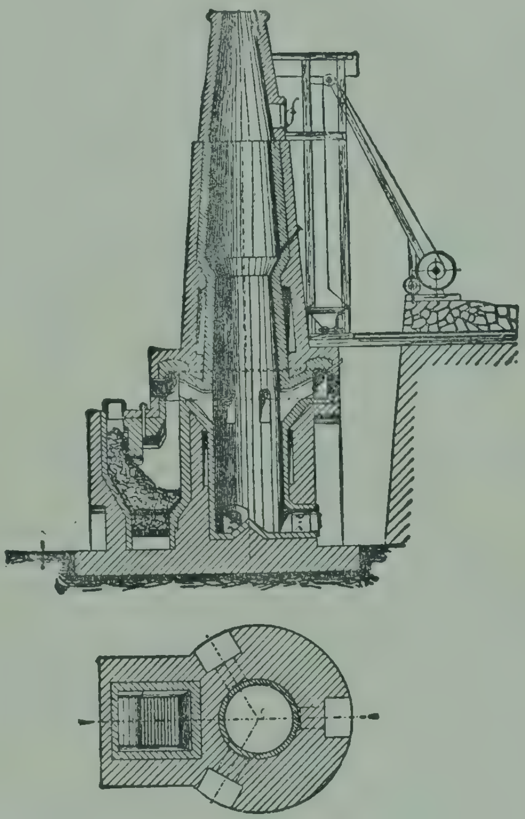


FIG. 4.—Schmatolla's Kiln.

These poor limes do not "set" under water, and must therefore not be confounded with the hydraulic limes which also slake slowly and with little change of volume, but which sooner or later set under water. A good sample of common lime should contain from 85–98 per cent. of calcium oxide. The following are some typical analyses:—

	Buxton Lime.	Building Lime.	Blue Lias Lime.	Dolomitic Lime.
Lime (CaO)	98.72	51.10	63.43	46.72
Insoluble residue	0.71	13.20	2.39	2.94
Combined silica (SiO_2)		10.34	14.17	
Magnesia (MgO)	0.46	1.04	1.54	32.60
Alumina (Al_2O_3)	0.11	1.64	6.79	1.90
Ferric oxide (Fe_2O_3)		0.21	2.34	
Sulphuric anhydride (SO_3)	...	8.00	1.63	0.92
Carbonic anhydride (CO_2)	...	14.47	3.64	3.27
Water (H_2O)	...		2.69	11.65
Alkalis and loss	...		1.38	
	100.00	100.00	100.00	...

For building purposes lime is made into mortar (see p. 125). In addition to this use, however, it is employed for softening water, as a dehydrant, in the defecation of sugar, and in all chemical industries where a cheap base is required.

HYDRAULIC LIME

Limes containing from about 15–30 per cent. of clayey matter (aluminium silicate) are called **hydraulic limes**, those containing over 20 per cent. being known as **eminently hydraulic.**

When treated with water these limes slake slowly and the increase in volume is small. When a paste made from such a lime is immersed in water it sets after a few days and then slowly hardens to a stony consistency. It is because of this property of setting under water that these limes are known as hydraulic. If the amount of clayey matter is only about 8–14 per cent. the lime is termed **moderately hydraulic**; such limes slake rather more readily than the true hydraulic limes and with a greater evolution of heat and a greater increase in volume; when made into a paste they set under water after two or three weeks, but never become very hard.

These hydraulic limes owe their peculiar properties to the formation of calcium silicates, aluminates, and perhaps alumino-silicates during calcination.

Hydrated limes may be compared to mixtures of crude Portland cement and common lime.

Hydraulic limes are prepared in the same manner as common lime, but limestones containing siliceous and clayey matter are used for the raw material. Care must be exercised in the choice of kiln employed, because such clayey limestones readily become partly fused and spoilt. The temperature must therefore be carefully regulated, and the kiln must be one which will permit of this regulation.

Chaux de Theil.—This eminently hydraulic lime has been very largely used by French engineers, especially for marine work, such as the harbours of Port Said and Suez.

It contains about 62–65 per cent. of calcium oxide, 15–22 per cent. of silica, 2.5 per cent. of alumina, 1.5 per cent. of magnesia, and small quantities of iron oxide, alkalis, etc.

Grappier Cements or Ciment Grapier.—In France hydraulic limes are slaked at the lime works and then passed through sieves. The hard lumps (*grapier*) which are left on the sieve consist partly of still unchanged limestone and partly of calcium silicates, and perhaps alumino-silicates. They are collected and finely ground, the resulting cement being known as **ciment grapier** in France and as **grappier cements** in England.

The composition and quality of these cements are very variable, for they depend upon the proportion in which the two kinds of material exist in the original lumps, the calcium carbonate being valueless as a cementing material. The following analysis is typical of a grappier cement:—

Analysis of a Sample of Grappier Cement. (Le Chatelier.)

SiO_2	26.5
Al_2O_3	2.5
Fe_2O_3	1.5
CaO	63.0
MgO	1.0
Alkalis	n.d.
SO_3	0.5
CO_2 and H_2O	5.0
	100.0

Scott's Selenitic Cement (Scott's Cement).—This cement is prepared from feebly hydraulic limes by the addition of plaster of Paris or sulphuric acid, by adding 5 per cent. of ground plaster of Paris to the lime, and finely grinding the mixture.

Sulphates have no effect upon pure lime; eminently hydraulic limes, however, are considerably improved by this treatment, though the feebly hydraulic limes are the best to employ for the preparation of selenitic cement. According to Scott's theory the gypsum in solution is deposited upon the lime particles, thus retarding the access of water to the lime, so that the hydration of the latter takes place much more slowly than it would otherwise do, and with but little evolution of heat or increase of volume.

Selenitic cement, when prepared according to Scott's process, has a warm buff colour, sets rapidly, and soon becomes hard. Although it is an improvement upon ordinary hydraulic lime, its use has not become general because it is unsuitable for work which is exposed to the weather, and especially to the action of salt water, and also because of the superior qualities of Portland cement.

PUZZUOLANIC CEMENTS

A pure lime may be converted into a hydraulic lime by adding suitable substances containing naturally or artificially roasted silicates. Thus, such materials as burnt clay, roasted shales, and brick dust may be used for this purpose, but the most important substances employed for the purpose are naturally occurring siliceous materials of volcanic origin, such as **puzzuolana, trass,** and **Santorin earth. Puzzuolana** is a volcanic tufa found in various parts of Italy, including Puzzuoli, near Naples, from which it derives its name. The colour varies from white to nearly black, and the composition is also very variable. Part of the silica is capable of readily combining with lime in the presence of water, forming a durable silicate. **Trass** is a similar material which is found in the Eifel district, on the west bank of the Rhine. It is largely used in Holland. **Santorin earth** is also a volcanic ash which occurs in the island of Santorin, in the Greek Archipelago. It contains a larger proportion of silica than puzzuolana or trass.

Instead of the natural materials just mentioned, burned clay, *e.g.*, broken tiles or crushed bricks or certain kinds of slag may be used (see below).

The finely ground puzzuolana or other "acidic" silicate is mixed with ground lime or with hydrated lime in suitable proportions. When required for use, water is added to the mixture.

These cements differ from other calcareous cements in not requiring to be heated during the process of manufacture.

The ancient Roman cements belonged to this class, but the modern so-called Roman cement (see p. 85) is of quite a different character.

Most puzzuolana or similar cements are generally a pale bluish grey in colour, but those made from slag may sometimes be brown on account of the presence of manganese in the slag. They contain a much smaller proportion of lime than does Portland cement. The specific gravity is low, never exceeding 2.8, and the tensile strength is considerably less than that of Portland cement. These cements are slow setting, generally taking at least five hours for the final set to take place, but they attain their greatest hardness in less than a year, sometimes, indeed, within the first month.

The setting time can be hastened by the addition of puzzuolanic materials, such as burnt clay, or by adding caustic soda, potash, common salt, etc., either in the form of an aqueous solution or in the dry stage, at any stage of the process of manufacture.

They stand the boiling and steaming tests very well. These cements are useful for mass concrete and for subaqueous work such as sea walls, but are generally inferior to Portland cement.

SLAG CEMENTS

Slag cements are a variety of puzzuolanic cements in which certain kinds of slags form the siliceous ingredient.

The slags used for the purpose of making cement are fusible silicates and aluminates, and perhaps alumino-silicates, formed by the combination of the fluxing materials with the gangue of the ore during iron smelting operations. The composition varies considerably so that all slags will not serve for the manufacture of slag cement, but only those of certain types can be employed for the purpose.

Blast Furnace Slag is the one chiefly used for this purpose. Prior to use, the slag must usually be granulated and dried, and then mixed with lime.

The Granulating of the Slag.—This is usually carried out by allowing the molten slag as it issues from the furnace to fall into a rapidly running stream of cold water, by which means it is broken up into fine particles known as **slag sand** and rendered hydraulic, and a part of the sulphur is removed as sulphuretted hydrogen.

This sudden cooling of the slag is necessary because slag which is allowed to cool slowly and is then ground to powder does not produce such good cement.

At Vitry, in France, the slag is granulated by impinging a jet of water against the molten slag as it issues from the furnace. The granulated slag is then dried and sieved, after which it is passed through six grinding mills of different types and again sieved, and is finally mixed and ground with the slaked lime in ball mills. In **Bosse & Wolter's** method of preparing slag cement, the grinding is carried out in a closed ball mill, called the **Homogeniser,** of the usual construction (see p. 94). The charge, consisting of one part by weight of dry slaked lime and three parts of dry granulated slag, is passed into the drum through a hollow trunnion. The aperture is then closed, and the drum slowly rotated about its axis until the materials are thoroughly mixed and ground, when a door in the outer lining is opened, and the finished cement ejected into bags or barrels. The cement does not need any further treatment, but is then ready for market.

The wet granulated slag must be fully dried or it will react prematurely when mixed with the lime.

Various forms of drier are in use for this purpose.

The **Ruggles-Coles drier** shown in Fig. 5 consists of two concentric steel cylinders capable of revolving about their slightly inclined common axis. The cylinders are connected at the middle by means of cast-iron arms, and at each end by means of adjustable arms. The inner cylinder projects beyond the outer at the upper end, and passes into a stationary air chamber which is connected to the hot air flue of the furnace. The lower end of the cylinder is also connected, by means of an opening in the bottom, to a second stationary air chamber, which is provided with a damper in order to regulate the temperature. The hot gases are drawn by means of an exhaust fan through the inner cylinder, then back through the annular space between the two cylinders, and finally through a flue leading to the exhaust fan, the direction of the current being shown in the figure by means of arrows. The wet granulated slag is charged through a shoot into the space between the cylinders, and as the latter revolves, it is carried around by means of scoops attached to the inner surface of the outer cylinder, and to the outer surface of the inner cylinder, and is dropped from the surface of one cylinder to that of the other, the process being repeated over and over again as the material gradually descends to the lower end of the drier when it is discharged dry. The **Holst drier** consists of a cylinder in which a helical screw revolves on a hollow central shaft. The slag is automatically fed into the cylinder and is slowly carried along by means of the revolving screw. The drier is heated by means of a fireplace beneath one end, and the hot gases pass under the cylinder to the other end, and then through the hollow shaft of the screw in the opposite direction to the slag to the stack. Similar driers are shown under **Manures**, p. 35.

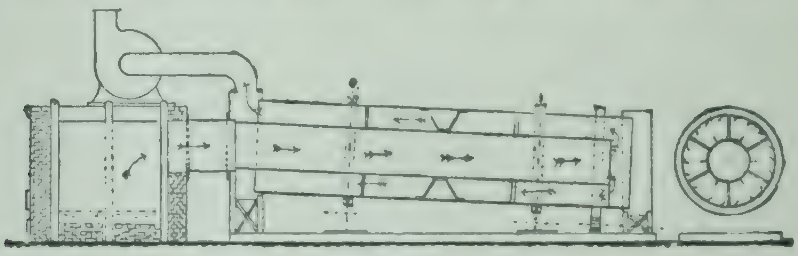


FIG. 5.—Ruggles-Coles Drier.

Mixing and Grinding. The granulated and dried slag is now mixed with carefully slaked lime, the proportions taken depending upon the composition of the slag. The lime used is generally common lime, but hydraulic limes are employed at some American, French, and German works. The lime must be slaked and sieved before mixing with the slag, and all material which fails to pass through the sieve should be rejected.

The mixture is then ground to an impalpable powder. The usual practice is to pass the mixture of dried granulated slag and slaked lime into the mixer, from which it is conveyed to the tube mills (p. 94) to be ground.

Instead of lime, Portland cement clinker is now generally employed, and the product is known as Blast Furnace Portland Cement. (See *British Standard Specification*, No. 146.)

Blast furnace cement is more closely allied to concrete than to Portland cement. The slag behaves as an acid and combines with the lime liberated when the cement is wetted, forming a puzzuolanic cement. It differs from concrete in requiring the addition of aggregate though not so much as can be added to Portland cement.

In a 3 : 1 sand : cement concrete, a blast furnace cement will produce briquettes which have the same strength as that required for Portland cement; the difference is chiefly noticeable when very lean mixtures of aggregate and cement are used.

Passow's slag cement, which was patented in 1901, is prepared by blowing air into the liquid slag as it issues from the blast furnace, by which means it is granulated. The material thus obtained is finely ground. Only very basic slags can be employed for this purpose.

A process of preparing cement has been devised by **Snelus,** in which the slag is calcined in a furnace after being granulated in the usual manner, by which means part of the calcium sulphide is oxidised to sulphate, and part decomposed with the evolution of sulphuretted hydrogen.

Modifications of these processes are used at the present time for the preparation of slag cements, slags from either white or grey iron being employed for the purpose. Instead of granulating the molten slag by letting it fall into water, it is often sprayed with a solution of alum or other salt, and then allowed to fall upon rapidly rotating drums, the fine globules of slag which are thrown-off by centrifugal force being cooled in air. The granulated slag is then finely ground in ball and tube mills (see p. 94), a little lime and gypsum being added in order to regulate the setting. A German cement, which is composed of 70 per cent. of Portland cement (made from slag and limestone) and 30 per cent. of granulated slag, is known as **Eisen-Portland-Zement, or Iron Portland Cement.** Highly basic slags are employed for its manufacture.

Cements are also prepared from blast furnace slag by calcining an intimate mixture of the slag and lime to incipient fusion, and finely grinding the clinker thus produced. These cements, however, although made from slag, are true Portland cement (see p. 87), and cannot therefore be classed with the puzzuolana or slag cements.

NATURAL CEMENTS

The natural cements are obtained by burning naturally occurring clayey or argillaceous limestones, and finally grinding the burnt material, a preliminary mixing and grinding sometimes being necessary before burning.

The first of the natural cements was prepared by **James Parker** towards the end of the eighteenth century. It was known at first as **Parker's cement,** but was afterwards called **Roman cement,** by which name it is still known.

Roman cement is made from the septaria nodules found in the London clay off the isle of Sheppey, and at other places along the Kentish coast. Later on similar nodules were obtained from the Hampshire coast, Harwich, Yarmouth, and other places. These septaria consist of an argillaceous limestone traversed by fissures filled with calcareous spar. The composition is very variable, the nodules from Sheppey and Harwich containing about 60–70 per cent. of calcium carbonate, 18–20 per cent. of silica, 6–10 per cent. of alumina and small amounts of magnesia and iron oxide. The nodules are first calcined at a temperature below the clinkering point in conical kilns, and the clinker thus obtained is then crushed and very finely ground, when it is ready for use.

The cement clinker may be kept unchanged for a considerable time, but after it has once been ground it deteriorates rapidly in contact with moist air, and should therefore be used as soon as possible after manufacture. **Medina cement** is a variety of Roman cement which is made from a stone found in the Isle of Wight.

Roman cement is reddish brown in colour. The specific gravity is about 2.5–3. When mixed with water it sets very rapidly, a good neat cement taking about ten minutes to set in air, and from a quarter of an hour to an hour to set under water, but it does not become so hard and stony as Portland cement.

It is a good hydraulic cement, and, on account of its property of rapid setting, is very useful for the protection of slow setting Portland cement concrete, etc., from the action of waves in marine work. For most purposes, however, it has been almost entirely superseded by Portland cement.

Continental Natural Cements.—About the same time that Parker introduced his cement in England a French military engineer named **Le Sage** prepared a similar material, which he named **plaster cement**, from the nodules found at Boulogne-sur-Mer. This cement must not be confounded with the true plaster cements which consist of calcium sulphate (see p. 113), as it was of practically the same composition as Parker's Roman cement. Similar cements have since been prepared at **Pouilly** (1829), **Vassy** (1831), and other places. These French quick-setting cements are prepared in much the same way as Roman cement, which they closely resemble. **Vassy cement** is very dark in colour on account of the large amount of iron which it contains, and is very quick setting when freshly burned.

In addition to these cements of the Roman cement type natural cements are also made in most European countries from naturally occurring argillaceous limestone rock of very variable composition. The stone is burnt without any preliminary treatment, and the resultant cement is consequently very variable in composition and quality. These cements are known as **natural Portland cements** and resemble true Portland cement both chemically and in physical properties. They are, however, of lower specific gravity (about 2.1-3.10), more quick setting and less strong. The district of Tournai, in Belgium, is the most important centre of this industry. True Portland cement is also made from the same rock by adding the required amount of limestone, calcining to incipient fusion, and grinding the clinker thus obtained.

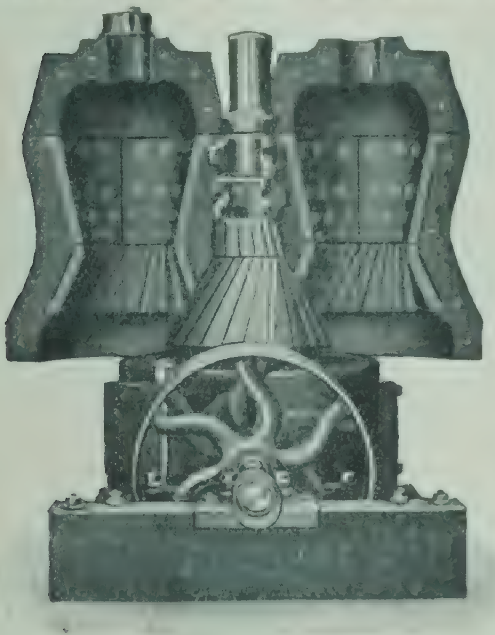


FIG. 6.—Cracker of the Coffee-Mill Type.
A rotary fine crusher supplied by the Sturtevant Engineering Co. Ltd., London.

American Natural Cements.—Before the introduction of the manufacture of Portland cement these natural cements were of great importance in America, but their manufacture has to a large extent fallen off. The raw material from which they are made is a clayey limestone containing about 13-35 per cent. of clayey matter and known as **cement rock**. According to **Cummings** the American natural cements may be divided into two classes according to whether they contain a preponderance of bisilicates or of trisilicates. Those of the first class are calcined at a higher temperature than those of the second class (which resemble Roman cement), and more or less ordinary limestone is generally added to the cement rock before calcination. The cements of the first class are known in America as **natural Portland cement**, but the term is inappropriate because the composition of Portland cement is practically the same whatever the raw materials from which it is made, so that when limestone is added in order to bring about a correct composition, a true Portland cement is obtained, and when no limestone is added the resulting cement usually contains from 10-15 per cent. less lime than does modern Portland cement. Of the cements of the second, or trisilicate, class, the best known is **Rosendale cement**. The raw material from which this cement is made is an argillaceous magnesium limestone which extends along the Appalachian range. The stone is blasted and conveyed in trucks to the continuous draw-kilns, which are charged with alternate layers of the cement rock and small coal; a portion of the charge is withdrawn every twelve hours, and fresh layers of stone and fuel added as the charge descends the kiln. The burnt stone is carefully picked over and any underburnt lumps returned to the kiln. The properly calcined material is broken up into small pieces about the size of a hazel nut in rotary mills of the coffee-mill type, known as **crackers**, such as that shown in Fig. 6, and then ground to such a degree of fineness that about 95 per cent. will pass through a sieve containing 2,500 meshes per square inch. The cement is finally packed in paper-lined casks, when it is ready for use.

Rosendale cement contains a large amount of magnesia, whilst the silica and alumina are comparatively low. Thus, samples of this cement contain from about 15-18 per cent. of magnesia, about 18-25 per cent. of silica and about 2-4 per cent. of alumina. According to Gillmore the average tensile strength of the neat cement is 104 lbs. per square inch after seven days, and the average crushing strength after the same period is 546 lbs. per square inch.

Louisville cement is made from the cement rock obtained at Louisville, in Kentucky. It is similar to Rosendale cement, but contains less magnesia, averaging about 9 or 10 per cent. of this constituent. With the exception of the temperature of calcination, the method of manufacture of all the American natural cements follows much the same course as that of the Rosendale cement.

PORTLAND CEMENT

Portland cement was first made by **Joseph Aspdin** (Patent No. 5,022, 1824), a bricklayer of Leeds, who gave it the somewhat misleading name by which it is still known, probably from a fancied resemblance to Portland stone. The cement was originally prepared by lightly calcining a mixture of lime and clay, and grinding the product, and it was therefore a very different material from that made at the present time. The manufacture of this cement has been developed by a large number of investigators, and is at the present time by far the most important of the hydraulic limes and cements, its superiority over all the others, both as regards strength and durability, having led to its use becoming greatly extended. This cement is the finely pulverised product obtained by heating an intimate mixture of calcareous and argillaceous materials to incipient fusion, and grinding the resulting

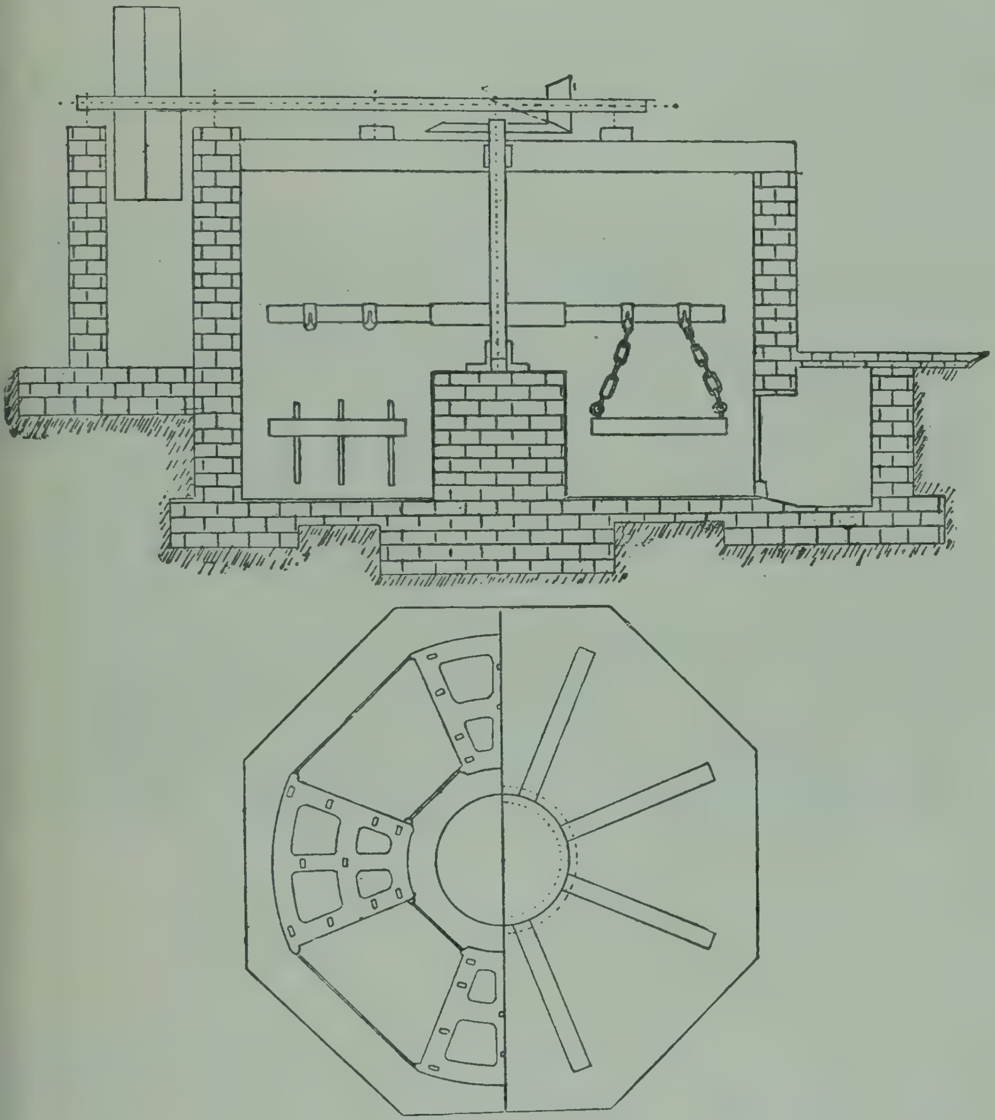


FIG. 7.—Wash Mill.

clinker. There is a very wide range of raw materials available for this purpose, such as limestone, chalk, cement rock, marls, clay, shale, slate, blast furnace slag, and so forth. The proportion of the materials taken must, however, be so adjusted as to yield a mixture containing about 75 per cent. of calcium carbonate and 25 per cent. of aluminium silicates and free silica.

Mixing the Raw Materials.—The raw materials must not only be mixed in the correct proportions, but the mixture must also be uniform and in a fine state of division. This is brought about by one of three systems known as the **wet**, **semi-wet**, and **dry** processes.

The Wet Process.—This is the original process, and is now almost obsolete. It is, however, still used at some works which employ soft, wet, raw materials, such as chalk and river mud or clay. The materials, without any previous drying, are mixed in the proper proportions with a sufficient quantity of water, and reduced to a fine mud, called the **slip** or **slurry**, which contains about 80 per cent. of water.

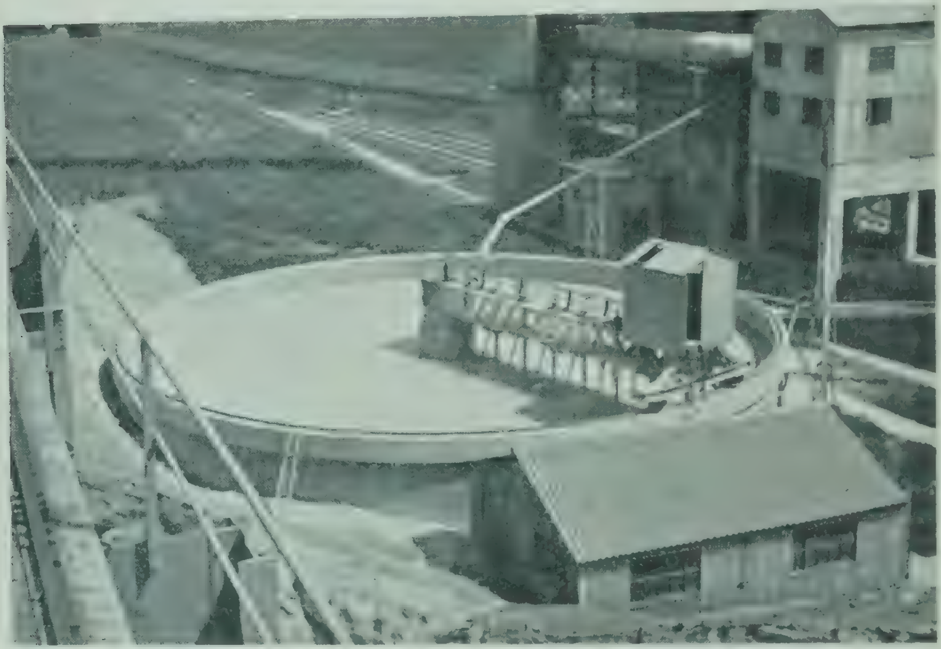


FIG. 8.—Horizontal Slurry Tank.

(From "Cement in the Making," by courtesy of the Cement and Concrete Association.)

This mixing is usually carried out in a **wash mill.**

This consists, as shown in Fig. 7, of a circular or octagonal brickwork (or concrete) tank, at the bottom of which is a short central pier supporting a vertical shaft. This shaft is rotated by means of a pair of bevel wheels, and carries radial arms from which are suspended iron or steel harrow frames, joined together by means of tie-rods, and carrying the steel tines. Finally, there are outlets fitted with gratings or sieves for the passage of the slurry at intervals around the circumference of the tank. A modern mill of this type usually has a diameter of about 30 ft., and the harrows perform twenty-four revolutions per minute. In a less common type of wash mill the harrows are held in frames which are secured to the central shaft. The raw materials are usually charged into the mill from skips or tipping waggons, and the water is run in through a pipe.

After having been churned to the correct consistency, the slurry is run off through the gratings or sieves into troughs leading to large reservoirs or **backs**, where it is allowed to settle, a process taking some weeks. The water is got rid of partly by soaking a way through the soil, partly by an evaporation, but mainly by drawing off the clear supernatant liquid at intervals through a perforated board, known as the **peg-board.** When the slurry has become sufficiently dry it is dug out from the backs and dried ready for the kilns.

In more recent practice the waste heat from the kilns is used to dry the slurry for the next charge. When the wet process is used on the Continent the slurry is left in the backs until it is stiff enough to be plugged and made into bricks, and the latter are dried in **tunnel driers** (see p. 213).

The Semi-wet Process.—In this process, which is the one commonly used in England, the slurry only contains about 40 per cent. of water, and is therefore known as **thick slurry**; it is, however, sufficiently wet to be pumped. In America, where the old wet process has scarcely ever been employed, this method is known as the "wet" process, the term "semi-wet" or "semi-dry" not being used in that country.

Wash mills are employed in the semi-wet process as in the original method, but the final reduction is usually carried out in ball or tube mills. Usually a separate wash mill is used for each ingredient of the slurry. If a hard source of lime is used, such as limestone, the mineral is roughly crushed before feeding to the ball or tube mill. The usual modern practice with limestone is to crush first in a jaw crusher, illustrated in Fig. 11, and capable of handling lumps up to 4 ft. in diameter, down to a maximum size of 9 in. diameter. This material is then further crushed in a swinging hammer or cone crusher down to a maximum of 1 in. diameter, and it is then stored until required for the slurry making process. In this process a slurry of clay and water is pumped continuously through ball or tube mills, in which the crushed limestone is being ground. The proportions of clay, water, and limestone are determined by analysis and final adjustments to the composition are made by blending the contents of the vertical tanks or mixers used for storing the slurry. These may be agitated mechanically, as in Fig. 10, or by blowing compressed air through the slurry, or by combinations of mechanical and air agitation. When chalk and clay are mixed into slurry in separate wash mills, the slurry from both is pumped through a common ball mill or tube mill before passing to slurry storage tanks. The coarse sand, pebbles, and stone that separate out in the wash mills are removed by a series of scoops from the bottom of the tanks. The output of a modern wash mill is approximately 150 tons/hr. of material containing less than 5 per cent. of residue on a sieve with 32,400 meshes to the square inch. The slurry storage tanks, in the case of works using chalk and clay as raw materials, are usually large tanks up to 80 ft. in diameter and 12 ft. deep, partially sunk into the ground, and of capacity from 1,000 to 2,000 tons. They are fitted with a revolving scraper arm mechanism to keep the slurry in suspension, and to a uniform consistency. A photograph of such a slurry tank is shown in Fig. 8. Alternatively, as with the vertical tanks, agitation is by compressed air. Hourly samples are usually taken of the slurry to determine fineness, calcium carbonate, clay and water contents, and adjustments are made of the materials fed to the wash mills, or wet ball or tube mills, to ensure correct analyses and consistency of the slurry.

A diagram showing the modern semi-wet method of preparing slurry from chalk or limestone and clay is shown in Fig. 9.

Ram pumps of the three-throw type are usually employed for pumping the fine slurry from the mixers to the kiln, or to the drying floors if it is to be formed into bricks. Sometimes, however, worm conveyers are used for this purpose, especially on the Continent.

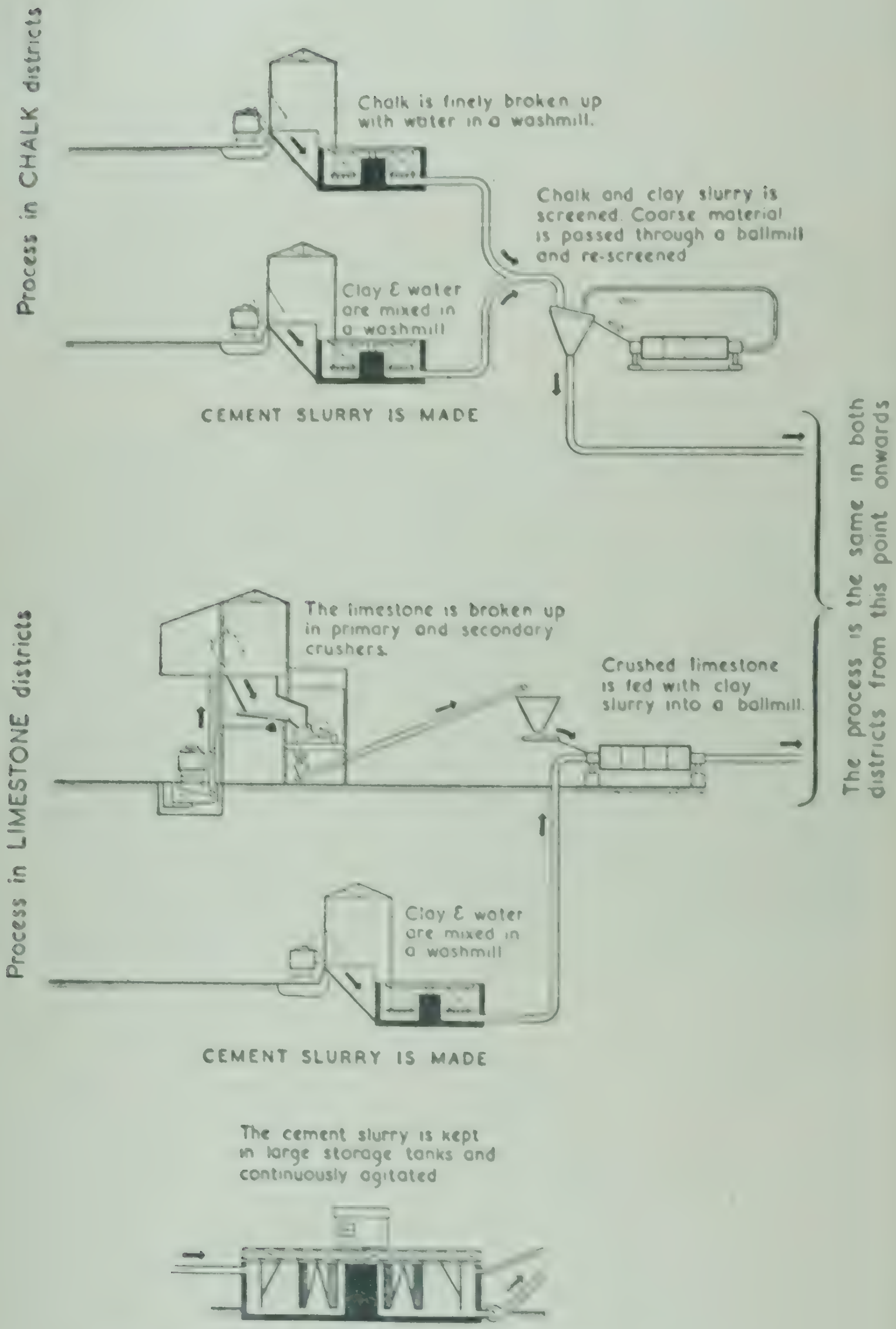

Process in CHALK districts
Chalk is finely broken up with water in a washmill.
Chalk and clay slurry is screened. Coarse material is passed through a ballmill and re-screened
Clay & water are mixed in a washmill
CEMENT SLURRY IS MADE
The process is the same in both districts from this point onwards
Process in LIMESTONE districts
The limestone is broken up in primary and secondary crushers.
Crushed limestone is fed with clay slurry into a ballmill.
Clay & water are mixed in a washmill
CEMENT SLURRY IS MADE
The cement slurry is kept in large storage tanks and continuously agitated

FIG. 9.—Cement Slurry Making Process.

(*From "Cement in the Making," by courtesy of the Cement and Concrete Association.*)

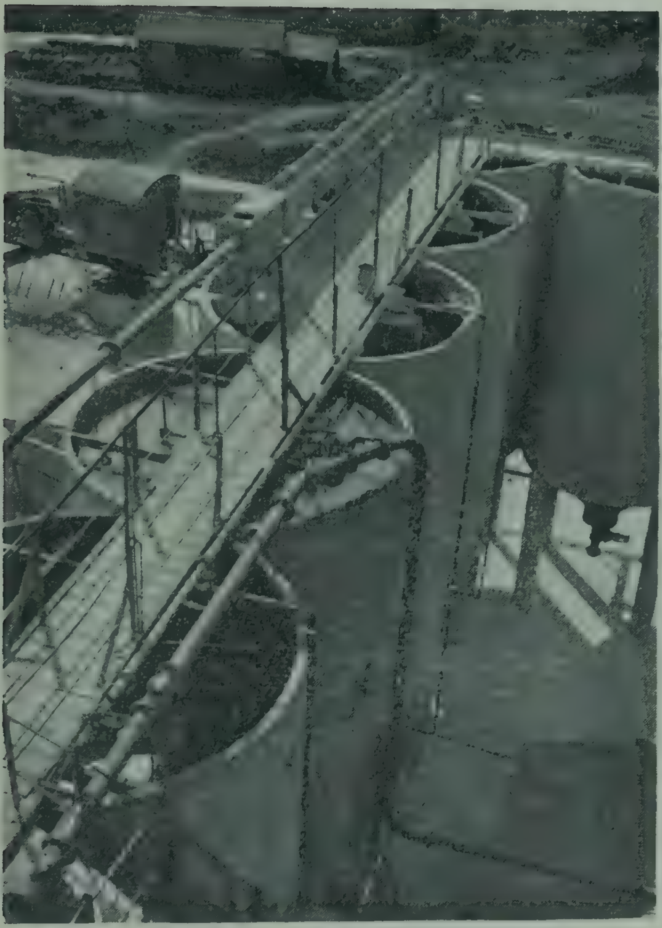


FIG. 10.—Vertical Slurry Mixing and Storing Tanks.
(From "Cement in the Making," by courtesy of the Cement and Concrete Association.)

The Dry Process.—This process was originated in England for the purpose of dealing with limestones and shales of the Lias formation, but its greatest development has been made abroad, and especially in America. The process is principally employed where hard materials such as limestone, shale, and slate are used, but it is also applicable to soft materials. In this process it is necessary to crush and dry the raw materials before passing them on to the mixer, as they must not contain more than 2 per cent. of water or the mills will become clogged.

Crushing.—Whenever possible, the crushing is carried out before drying, because this facilitates the latter process, but very wet, soft materials have to be dried first and crushed afterwards. The type of crusher used depends principally upon the character of the raw material. If the latter be hard and fairly dry it is usually crushed to about the size of a walnut, either in a machine of the **swing jaw stonebreaker** type or in a **gyratory crusher**, whilst if it be soft and moist it is usual to employ a **rotary crusher** of the **coffee-mill** (see Fig. 6) type or else a mill with **toothed hedgehog rolls**.

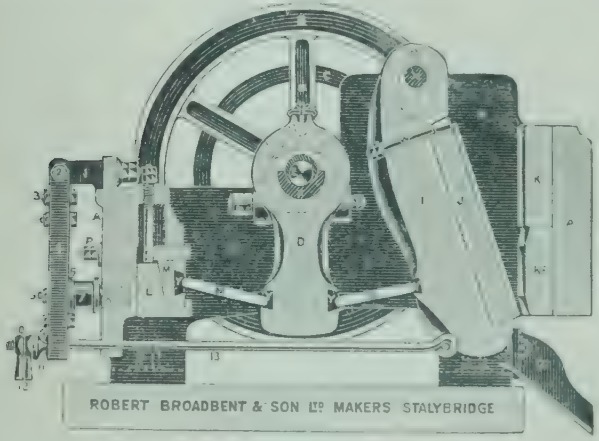


FIG. 11.—Section of Broadbent's Improved Blake Stonebreaker.

The swing-jaw stonebreaker is the oldest type of crusher, and most of the forms at present in use are modifications of the **Blake's stonebreaker** shown in section in Fig. 11. In this crusher, one of the jaws A is fixed whilst the other I is hinged; both jaws are faced with grooved plates of chilled iron or manganese steel J and K^1 K^2, and the hinged jaw is caused to swing backwards and forwards through a very small arc by means of a pitman D, which is alternately raised and lowered as the eccentric shaft E rotates. The size of the crushed material is regulated by railings or lowering the wedge L, and the return of the swing-jaw by the drawback motion, P, Q, R, S, T, U, V. In another design of this crusher, the **Blake-Marsden "frictionless lever" crusher**, the movable jaw is swung by means of a pitman and rocking lever. In another type of jaw crusher the movable jaw is worked by means of a lever and cam. The Wheeling Mould and Foundry Co. have recently introduced a modified swing-jaw crusher called the **Wheeling forced feed crusher**, in which a rolling motion is imparted to the jaws, thus increasing the crushing power and output. Gyratory crushers are generally used in America, but are not so popular in this country. A sectional perspective view of **Hadfield's gyratory crusher** is shown in Fig. 12. This crusher consists of a hopper-shaped shell N, beneath which is an inverted cone A, supported on a casing which also carries the driving machinery. The crushing cone R is attached to the hollow shaft T, which is supported on the spindle I by means of the ball and socket arrangement P, 12. The crushing cone is caused to gyrate by means of a bevel wheel with an eccentric boss G. The cone mantle S and the plate O which line the shell N are made of manganese steel. The stone is fed into the hopper where it is crushed by the gyrating cone, and then drops into the inverted cone A, from which it escapes from the crusher. The size of the product can be regulated by raising or lowering the central spindle I by means of a worm and worm wheel at the bottom of the machine. Rotary crushers or **crackers** of the coffee-mill type (see Fig. 6) are sometimes employed for crushing comparatively soft materials and also for reducing the size of the lumps of hard material as it comes from the more powerful crushers described above, but their use is not at all general in the manufacture of Portland cement. The most suitable mills for crushing soft materials are those with toothed rolls such as that shown in Fig. 13. This mill has two hedgehog rollers placed opposite one another; one of these is supported by sliding bearings in order that the distance between the rolls may be regulated. The size of the teeth used depends partly upon the character of the material to be dealt with and partly upon the size of the product.

Drying the Raw Materials.—At the present time **rotary driers** are almost universally employed. The simplest form of rotary drier is described under **Manures** (see p. 35).

The **Ruggles-Coles drier**, which is used to a large extent, is described on p. 84. When rotary kilns (see p. 99) are employed the waste gases from the latter are generally used to heat the driers instead of employing a separate furnace. Taking advantage of the hot dry atmosphere, the Californian Portland Cement Co. dry their wet clay without any artificial aid. During the summer the clay is ploughed up in patches and left to dry, after which it is brought to the works by rail and stored in bins. The kilns used normally are from 40 to 100 ft. long and are from 4 to 6 ft. in diameter.

Grinding. —The crushed and dried material is next submitted to fine grinding, the usual modern practice being to submit the material to a preliminary grinding in mills of various types, and then to finish pulverising the grit thus obtained in finishing mills.

Edge-runners, or heavy duty revolving solid bottom pan mills, are sometimes used for a preliminary grinding operation. A modern type will crush a 1,000 lb. batch in 12 minutes. The product from the pan mill is then usually passed on to a tube mill for fine grinding.

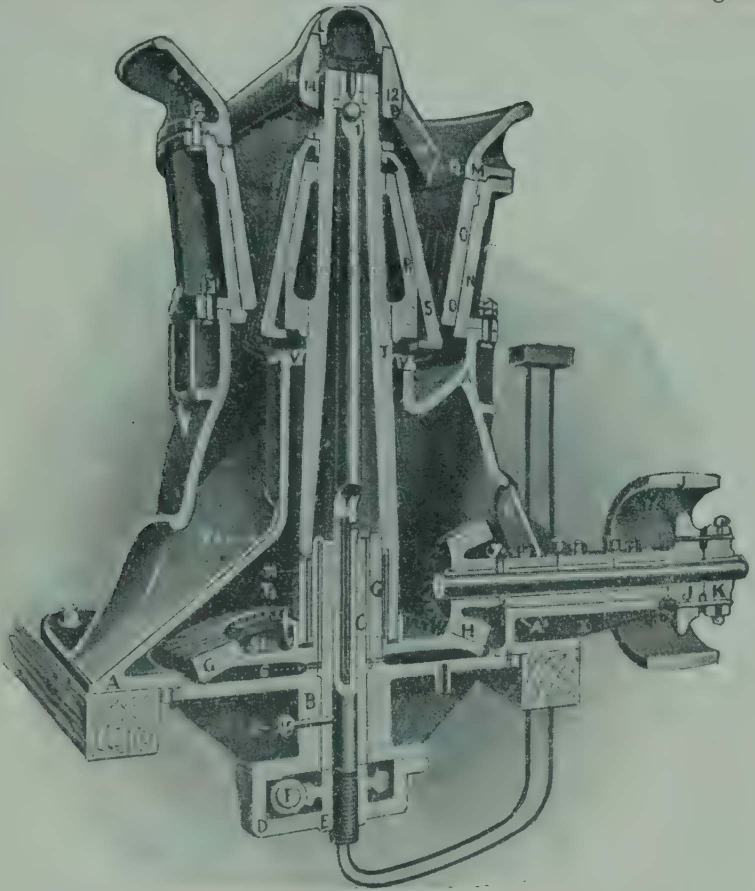


FIG. 12.—Hadfield's Gyratory Crusher.

Soft lumpy material, such as clay, is sometimes submitted to a preliminary reduction in machines of quite a different type. **Bar disintegrators,** described under **Manures,** p. 26, are in use. A machine which is capable of dealing with harder materials is the **Jeffrey pulveriser** in which the material to be ground is carried around by a spider, to which the hammers are attached, and crushed against the breaking plate until it is sufficiently reduced to pass through the grating at the bottom of the machine. Sometimes a **roller mill** is employed as an intermediary grinder between the edge-runner and the finishing mill. These mills are furnished with feed rolls which deliver the material at a uniform rate to the grinding rolls.

The **ball mill** was first introduced in Germany, and was originally intended for fine grinding, for which purpose it has not proved perfectly satisfactory, as it does not produce a sufficient quantity of very fine flour. It is, however, one of the best mills for primary reduction of the crushed material, and will probably supersede most of the other types of mill at present in use for this purpose.

Ball mills vary considerably in constructional details, but the principle has been explained on p. 24 under **Artificial Manures,** the **Abbé ball mill** being there described. The **Krupp ball mill,** shown in Fig. 14, has a circular drum composed of two wrought-iron side plates carried on a horizontal shaft. The inner circumference of the drum is built up of perforated plates of tough cast steel arranged so as to form steps. A perforated steel plate surrounds these grinding plates, forming a coarse sieve, outside which there is a fine sieve of brass or steel wire, the whole being enclosed in a sheet-iron case. The drum is charged with forged steel balls, and the material, which is fed in through a hopper at the side of the drum, is crushed by the balls which fall from step to step as the drum rotates. The ground material passes through the holes in the grinding plates on to the coarse sieve, which retains the larger particles, and allows the finer portion to pass through to the fine sieve, where the same process is repeated. The portion which succeeds in passing all the sieves then falls into the iron casing and is removed, whilst the coarser particles retained by the fine or coarse sieves are returned to the interior of the drum, where they are further reduced.

Modern ball mills are generally longer in relation to the diameter than the Krupp mill illustrated in Fig. 14. The shell is usually rolled from a single sheet of mild steel plate on mills up to 10 ft. by 10 ft. in size and the liner plates are made of heat-treated manganese steel, chrome steel, or cast iron secured by bolts to the shell. The end liner plates, discharge grids, and diaphragm plates are also of manganese or chrome steel. Ball mills, conical ball mills, and tube mills are all suitable for wet or dry grinding. The following table shows the usual commercial range of size, weight of steel balls, power requirements, and outputs of the three types of ball mills generally used in the cement industry. The tube mills are described on p. 97.

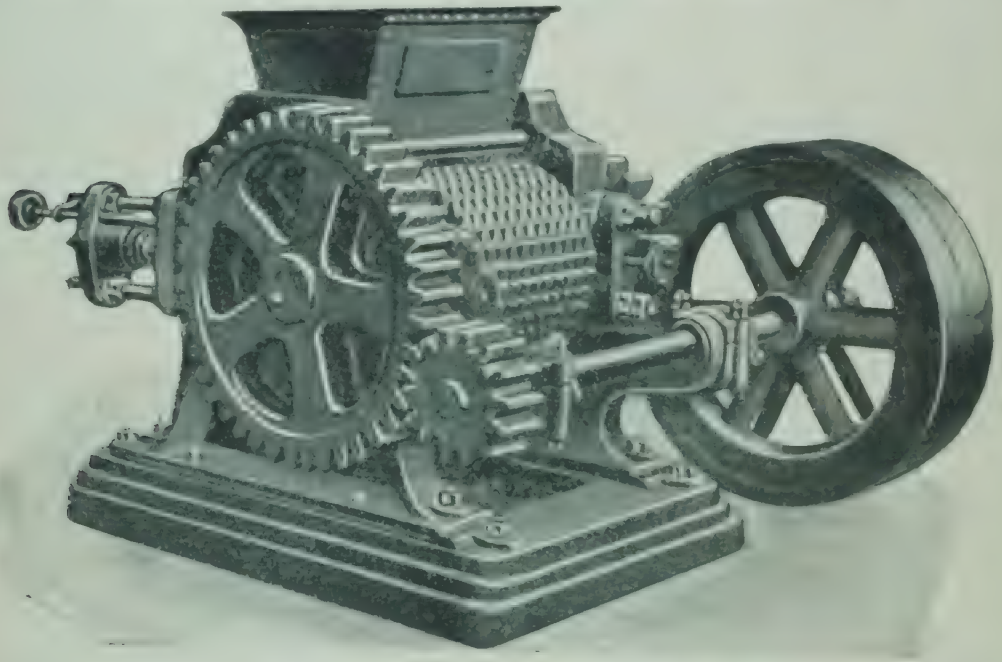


FIG. 13.—Roller Mill with Toothed Rolls.

CAPACITY OF BALL AND TUBE MILLS

	Diam.		Length.		R.P.M.	H.P. absorbed.	Wt. of balls, tons.	Approx. output of ground cement clinker per hr.
	ft.	ins.	ft.	ins.				
Conical Ball Mills—								
Min. - - -	4	0	1	4	32	20	1.7	1.5
Max. - - -	10	0	4	0	18	350	30.0	24.0
Normal Ball Mills—								
Min. - - -	3	0	3	0	30	15	0.4	1.0
Max. - - -	8	0	7	6	18	260	16.0	18.0
Preliminary Tube Mills—								
Min. - - -	5	0	5	0	25	38	3.25	2.5
Max. - - -	9	0	12	0	18	350	24.0	25.0
Finishing Tube Mills—								
Min. - - -	4	0	12	0	30	50	4.75	2.0
Max. - - -	7	0	30	0	120	500	37.0	20.5
Compound Tube Mills—								
Min. - - -	4	6	20	0	28	110	10.0	2.5
Max. - - -	8	0	44	0	20	1,100	72.0	20.0

It should be noted that the output of these mills depends upon the hardness or grindability of the material treated and the fineness or division of the finished product. Approximate outputs for cement clinker are given in the table, but for raw materials such as limestone, the output is several times as high as that for cement clinker. Whereas ball mills will grind up to [illegible] tons per hour of soft limestone or shale for a power consumption of approximately 30 H.P. per ton the same machine will only grind about 2.25 tons of cement clinker. In contrast, the wash mill converts clay or chalk to slurry for a consumption of about 7 H.P. per ton.

Various kinds of centrifugal **roller mills** are sometimes used for grinding the raw materials. In most cases the grinding is completed in one stage, the mill thus taking the place of the combined ball and tube mills.

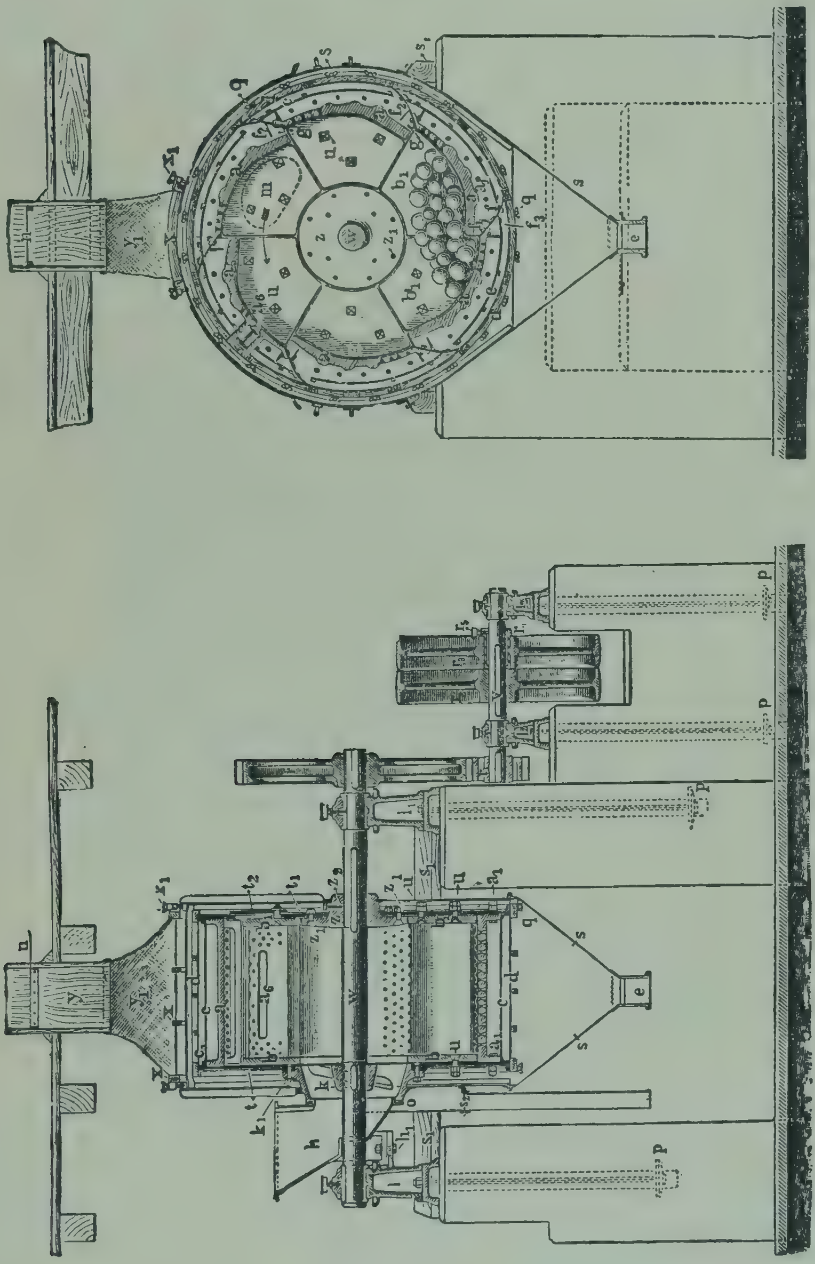


FIG. 14.—Krupp Ball Mill.

The **Griffin mill**, which is manufactured by the Bradley Pulverizer Co., is shown in section in Fig. 15. In this mill the roll 31 is attached to the shaft 1, suspended from the universal joint 9, which is connected to the horizontal driving pulley 17 by means of sliding bearings. The grinding chamber, in which the roll swings and rotates, consists of a base pan 24 containing a grinding ring, and a sieve frame 44 carrying a cylindrical sieve surrounded by a sheet-iron dust casing. Attached to the top of the sieve frame there is a conical shield 25 through which the shaft passes. The raw material is fed into the hopper 50 and is conveyed by means of the worm 49 into the base pan, where it is ploughed up by the shoes or ploughs attached to the bottom of the roll, and ground between the latter and the grinding ring. The finer particles are winnowed by the fans 7 and, after passing through the sieve, fall into a receptacle below, from which they are removed by means of a worm conveyer. A larger and more powerful form of this mill is known as the **giant Griffin**. The **Bradley three roll mill** is described on p. [illegible], under **Manures**.

In the **Kent mill**, the **Maxecon mill**, and the **Sturtevant ring roller mill**, the grinding pressure is produced by means of powerful springs; the last-named mill is described under **Manures** on p. 25.

In the case of all these mills, the ground material must either be further reduced in a finishing mill or passed through a separate sifting device, and the coarser particles returned to the mill for further grinding. The **Roulette mill**, which is shown in Fig. 16, is a centrifugal roller mill of a different type, in which the rollers are replaced by balls. These balls **8** are driven by the legs **7** of the driving disc **6** around the grinding ring, which is made in two parts **9** and **10**. The material is fed by means of the automatic feed **31** through the shoot **32** into the mill and ground between the balls and the grinding ring. The spider **3**, attached to the shaft **2**, carries the blades **4** and **5**, which form a fan and throw the ground material against the coarse sieve **11**, thus separating the coarser particles. The material is then sifted by the fine sieve **12**. The coarse particles retained by the sieves fall back and are reground, whilst the fine meal passes through the hollow standards into the receptacle below, and is finally removed by a worm conveyer. One of the latest mills used in the cement industry is the **Fuller Lehigh mill**. This is also a centrifugal mill in which balls are used instead of rollers. It is sometimes used for both fine and coarse grinding, but the manufacturers only recommend it for the former.

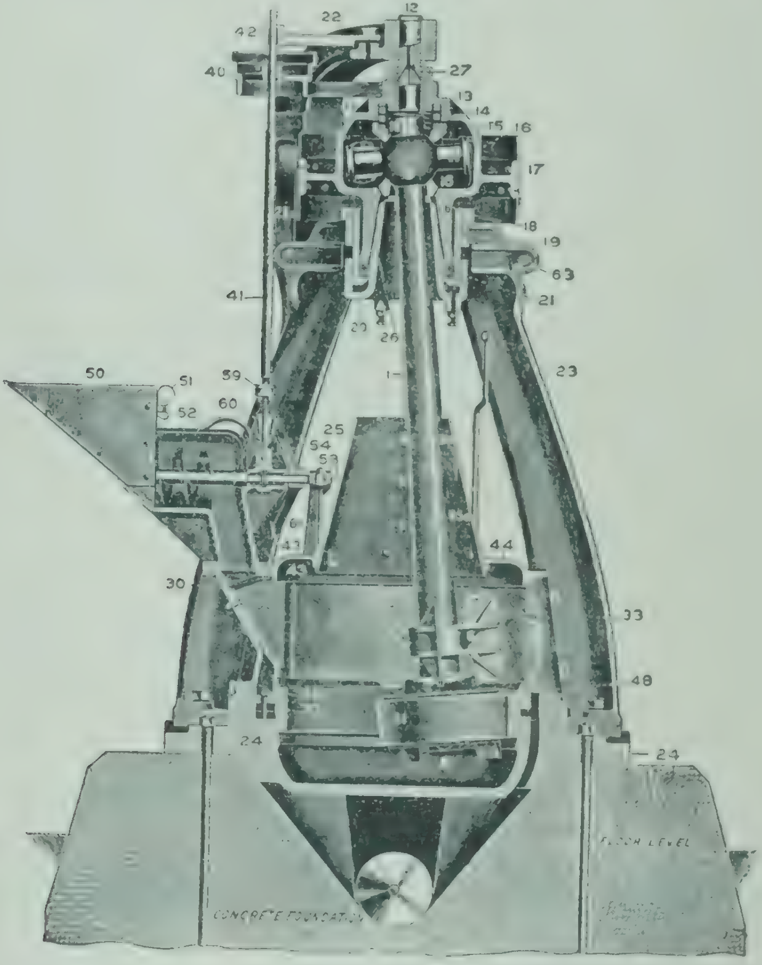


FIG. 15.—Section of Griffin Mill.

By far the most common form of finishing mill at the present time is the **tube mill**, which was introduced into the cement industry about 1895. This is described under **Manures** on p. 24. Among the types used in the cement industry may be mentioned the **Armstrong-Vickers** and **Newell's tube mills**.

These are designed on similar principles to the ball mills made by the same firms, and the **compound** or **multi-chamber** mills described below. The driving arrangement on the larger mills is from electric motor through a double reduction helical gearbox to a flexible coupling. Smaller machines are either driven by flat belts through counter shaft gearing, or by means of V-belts. Tube mills are commonly used up to 50 ft. in length and up to 8 ft. in diameter. They are sometimes divided into preliminary tube mills of relatively high output, and finishing tube mills of lower output.

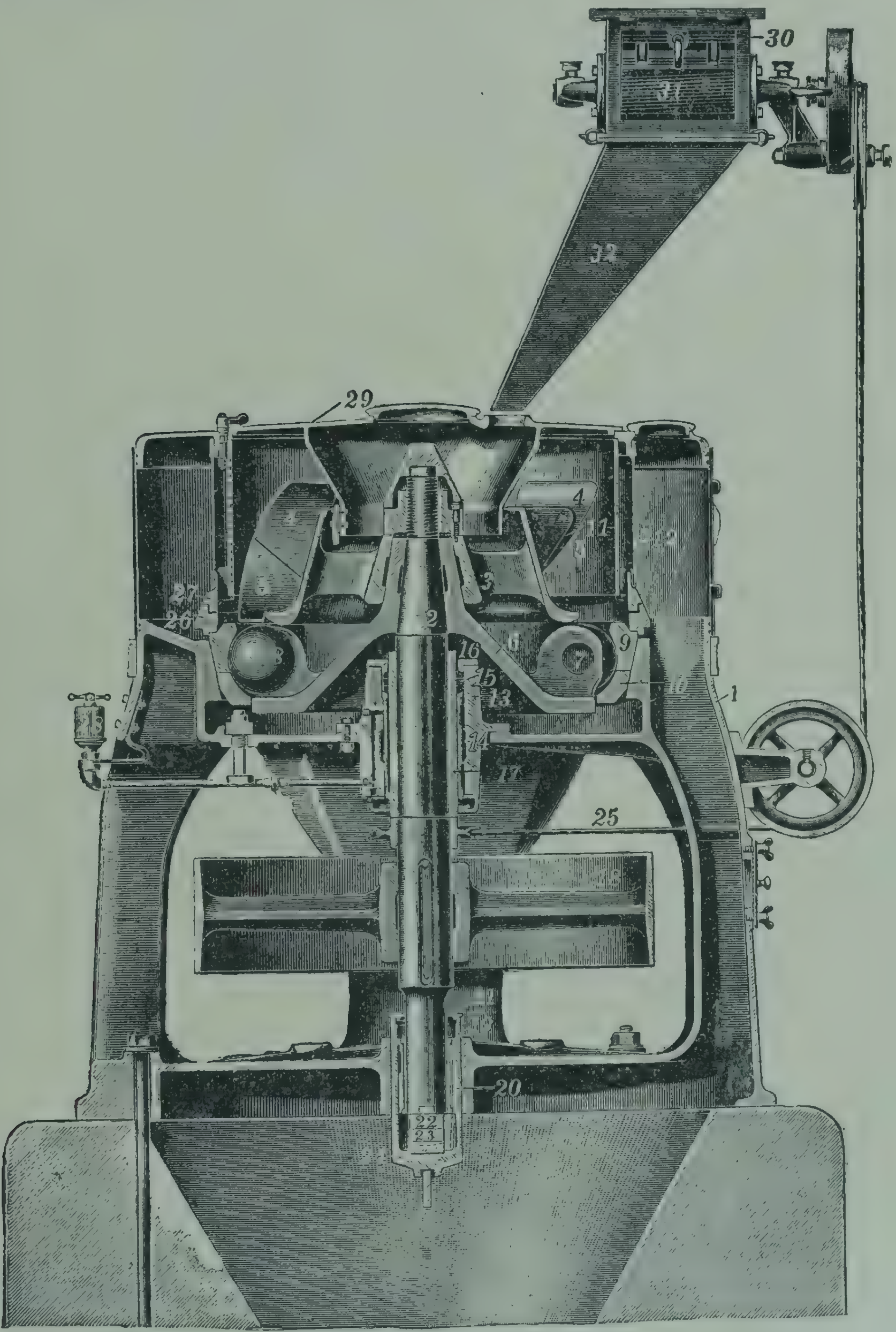


FIG. 16.—The Roulette Mill.

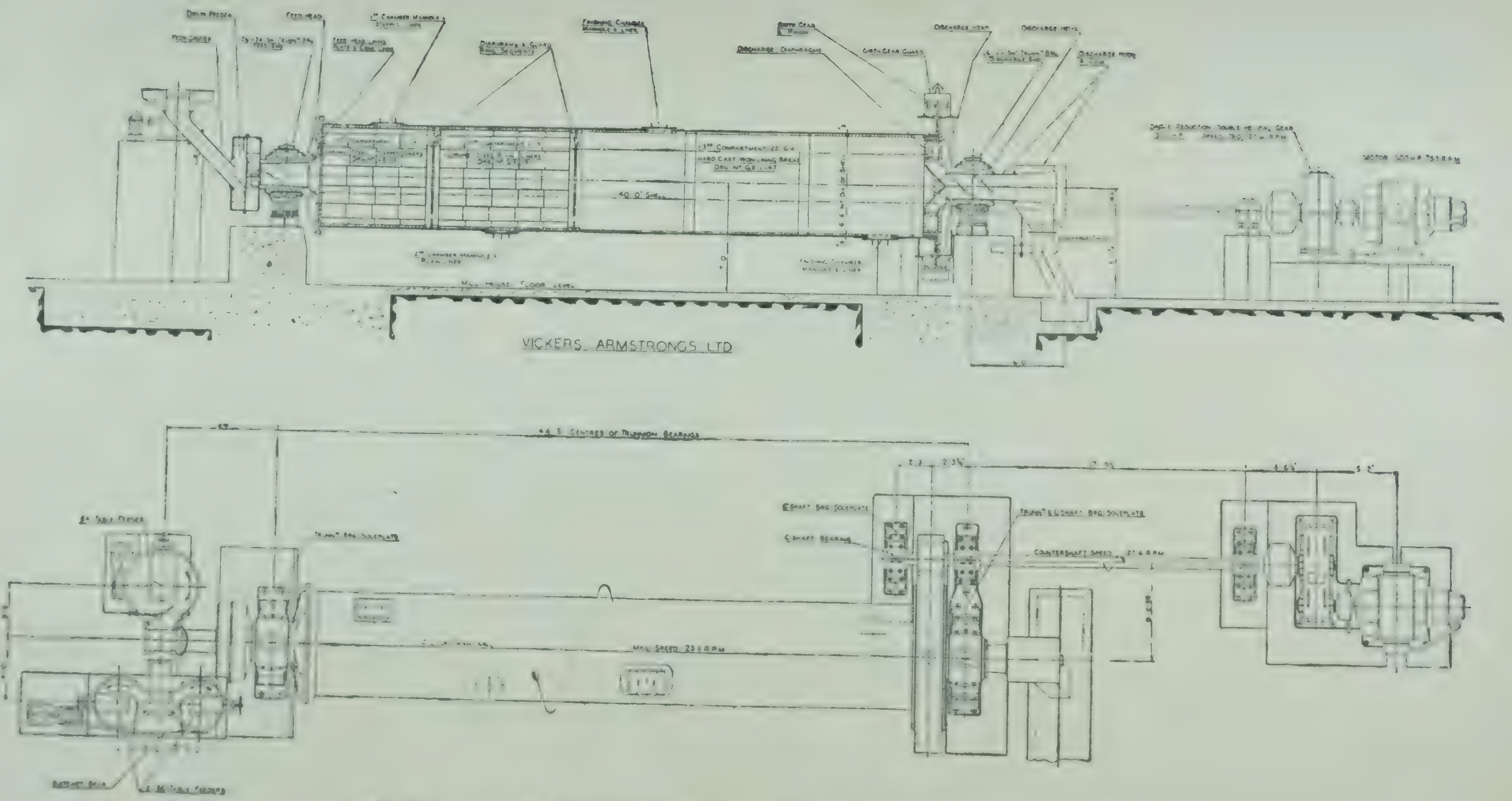


Fig. 17.—General Arrangement—Compound Tube Mill. (*Vickers Armstrongs Ltd.*)

Compound or Multi-Chamber Tube Mills

For the rapid grinding of cement, to a close specification, multi-chamber tube mills, containing from 2 to 5 independent grinding chambers, are now commonly used. This construction permits the grading of the grinding media, which is an advantage, since, as size reduction proceeds, smaller grinding balls are required, a different type of liner plate is also used in each compartment of the mill. A section of a Vickers-Armstrong compound tube mill is shown in Fig. 17.

The outputs and power consumptions of the various types of ball and tube mills have already been given in the table on p. 94.

MIXING

In suitable cases, as when the raw materials are fairly pure and of regular composition, they are mixed in the required proportions after drying and ground together. In most cases, however, the materials are passed separately through the coarse grinding stage and stored in separate bins, from which they are withdrawn by means of worms, weighed in automatic weighing machines, and discharged into a conveyer which mixes and carries the mixture to the finishing mills. The finely ground material from the finishing mills is technically known as **raw flour, raw meal,** or **compo**. It is conveyed to the storage bins or **silos** by means of spiral or other conveyers, and is tested on its way for fineness and composition, the necessary corrections being made in the latter if required.

In order to render the composition uniform the contents of the silo are kept stirred by means of some mixing device. The silo shown in Fig. 18 consists of a shell with a hopper-shaped bottom.

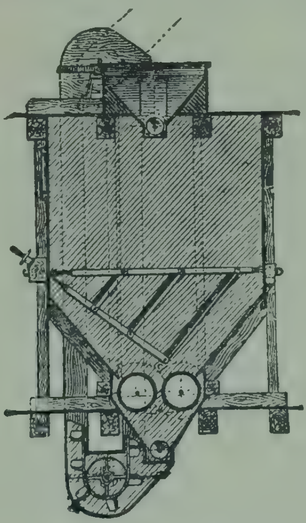


FIG. 18.—Mixing Silo.

The material is fed into the cell by means of a worm conveyer situated at the top, distributed by means of rollers along the trough of a second spiral conveyer situated at the bottom of the silo, and then returned to the upper conveyer by means of an elevator, the process being continued over and over again.

Sequence in Dry Mixing Process.—The normal sequence of events followed in the dry mix process up to the kiln is therefore—

(1) Rough grinding—usually by heavy gyratory crusher or jaw crusher.
(2) Hammer mills—or crushing rolls.
(3) Storage for crushed limestone, chalk, shale, or slag.
(4) Rotary driers to blending silos.
(5) Ball mills, followed by tube mills or multi-compartment tube mills.
(6) Dry mixed storage silos.

When rotary kilns (see below) are employed the dry raw flour is conveyed direct to the small storage bins which supply the kilns, but where stationary kilns (see p. 100) are used the raw flour from the mixing silos is made into *briquettes*.

In one method of briquetting the flour is conveyed from the silos to a pug mill, where it is ground up into a very stiff paste containing about 18–25 per cent. of water, and as it leaves the mill the paste is cut off into short lengths by means of wires, and moulded in a plastic brick making machine, one of which is shown in Fig. 19. The briquettes thus obtained are dried, generally by the waste heat from the kilns or in **tunnel driers.** In the latter method, which is chiefly used on the Continent, the bricks are stacked on waggons and slowly conveyed through tunnels from 100–120 ft. in length, through which a large volume of hot air is passed in the opposite direction to the waggons (see p. 227).

In another method of briquetting the flour is converted into a much drier paste containing about 8–10 per cent. of water, and this is made into bricks by stamping or pressing, in special briquette-making machines, such as those described in Vol. I., p. 22, under **Briquette Making.** Among machines used in the cement industry may be mentioned the **President Dry Press** and the **Eggette** moulding machine. The latter produces spherical blocks.

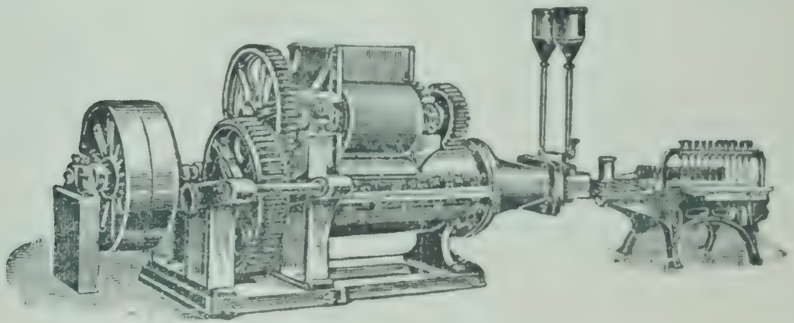


FIG. 19.—Plastic Brick-Making Machine.

Sometimes the raw material and fuel (usually coke breeze) are mixed together and formed into briquettes. In some cases a little lime is added to the raw material in order to increase its binding power, and natural cement has also been used for this purpose in America. Sometimes a combination of the wet and dry processes is employed, a dry flour being prepared from the hard material and a wet slurry from the soft. The two materials are then mixed in the correct proportion in a pug mill and made into briquettes.

Burning to Clinker. The mixed dry raw materials are now heated to the point of incipient fusion (*i.e.*, almost to white heat) in **kilns.** The modern kilns employed for this purpose vary considerably, but they may be classified under three heads, **rotary, moving grate,** and **vertical** kilns. The latter are usually of the *continuous* type, but *stationary* intermittent kilns are still used in some old works. The rotary kiln is the most important type and will therefore be described first.

THE ROTARY KILN

The **rotary kiln** is also the most popular type of cement kiln, especially in America, where it is rapidly becoming universal. It consists essentially of a steel cylinder, lined with fire brick, which is capable of being slowly rotated about an axis slightly inclined to the horizontal. The raw material is fed in at the upper end, and the fuel and air are injected at the lower end. The burnt clinker is also discharged at the lower end. The raw material may be prepared by wet or dry methods, but the latter is usually employed when one or both of the materials is of a hard nature. It is more economical to use a longer kiln when wet material is employed than when the latter is dry, because the waste gases can be utilised to remove some of the water.

At the present time the usual length of the cylinder is from 200–350 ft., and the diameter is from 7–12 ft., the largest in use being about 450 ft. long, and 12 ft. 6 ins. in diameter. Although the cylinders usually have parallel sides, they are occasionally made tapering at the end where the kiln enters the flue, and, frequently, the end portions are made of larger diameter than the rest, as shown in Fig. 20.

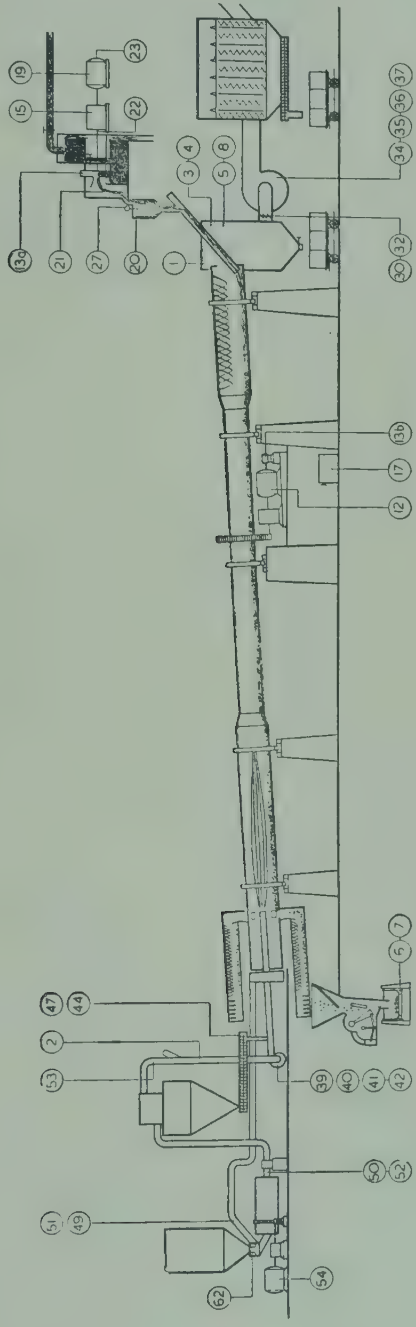


FIG. 20.—Cross section through rotary cement kiln with coal and air feed, slurry feed, driving mechanism, and dust extraction plant.

(From "Cement in the Making," by courtesy of the Cement and Concrete Association.)

The output of a rotary kiln operating the wet process varies from about 1,000 tons/week for the smaller kilns of dimensions 7 ft. by 200 ft. to 3,000 tons/week for the larger kilns of dimensions 12 ft. 6 ins. by 375 ft.

The cylinders are usually made of steel plate riveted to butt straps and lined with a suitable material. Ordinary stock bricks may be used to line the comparatively cool upper end of the cylinder, or this portion may be left unlined, and common fire-bricks may be used for the central portion, but for the hot lower end or burning zone these will not do, as, owing to the large percentage of silica which they contain, they behave as an acid towards the basic cement clinker, with the result that the lining is soon destroyed. Bricks containing about equal proportions of alumina and silica are often used for this portion of the lining; magnesia bricks have been employed, but although of a highly basic nature, have had to be abandoned because of their tendency to crack and shrink. Bauxite bricks have also been used to a limited extent, but have been found weak and friable. A cheap and efficient lining which is often used is a concrete made with about 2 parts of hard burnt clinker, and 1–1½ parts of cement. The clinker must be, at least, small enough to pass through a sieve with a half inch mesh. A layer of asbestos has occasionally been employed behind the fire bricks, but the plan is of doubtful value, and has not received much favour. It is usual to spread a protective coating of the clinker itself over the lining when starting the kiln. The cylinder is carried on two or three pairs of roller bearings, placed at a convenient distance apart. The roller bands or tyres, which are of steel, may be riveted directly to the cylinder, but in order to allow for the expansion of the latter it is more usual to make them about 3 or 4 in. larger in diameter, and to attach them to the shell by means of steel bridge pieces supported on blocks. The rollers upon which the tyres bear are fastened to sole plates. It was formerly usual to employ two pairs of rollers to support each tyre, but the modern plan is to use two single rollers (see Fig. 21).

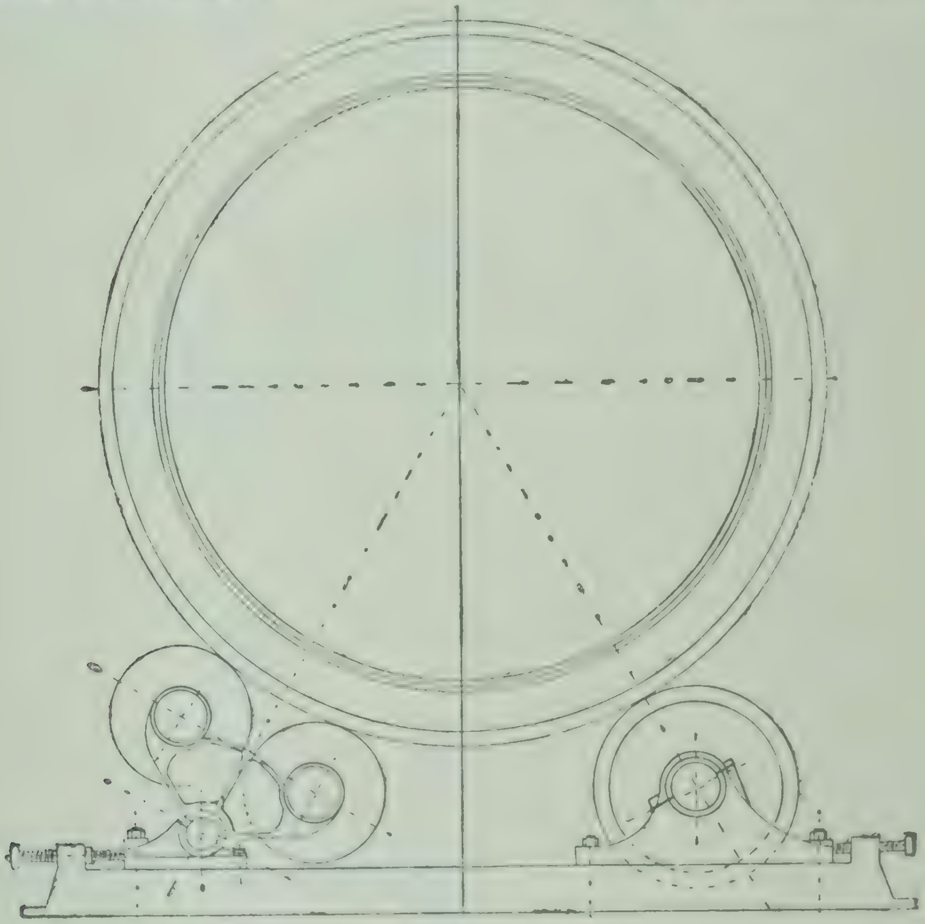


FIG. 21.—Forms of Bearing for Rotary Kiln.

The kiln is rotated by means of a split toothed wheel, which is usually attached to the cylinder in the same manner as the roller bands, or sometimes by means of tangential steel strips. The toothed wheel is actuated by a worm wheel driven by means of a suitable reduction gearing. The speed of rotation depends partly upon the slope of the kiln (which may vary between 3½ and 7 per cent.), partly upon the nature of the raw materials, and partly upon the thermal conditions inside the kiln; it usually varies between 20 and 60 revolutions per hour. In order to enable the feed, etc., to be under proper control, it is the common practice to employ some means of regulating the speed at which the kilns are driven. This may be done by means of separate motors provided with controllers for each kiln, but it is more usual to employ a three-speed gear, or to have pulleys of different diameters on the driving shaft.

At the upper end the cylinder terminates in a flue leading to a chimney. As the kiln gases are heavily laden with dust, it is necessary to pass them through some form of dust chamber in order to collect the dust before they reach the chimney. This dust collector usually consists of a settling chamber for the coarse dust, followed by a dust filter such as the Beth dust collector, shown in Fig. 22, or an electrostatic precipitator, as shown in Fig. 23.

The apparatus for the introduction of the raw material into the kiln is placed above the dust chamber. When the material is prepared by the semi-wet process the slurry is pumped from the mixers into a large storage tank, from which it passes into a small receiver, and hence along the feed-chute into the kilns. In some cases, however, the large tank is dispensed with. But when the material is prepared by the dry process, the flour may be fed in from the storage tanks by means of a worm conveyor in a water-jacketed case, as in the usual American practice, or it may be fed by means of a worm into a trough, along which it is carried by means of knives or arms attached to a rotating shaft. As the material travels along it is wetted by means of a perforated pipe placed over the trough, and finally falls in small lumps into a chute leading into the kiln.

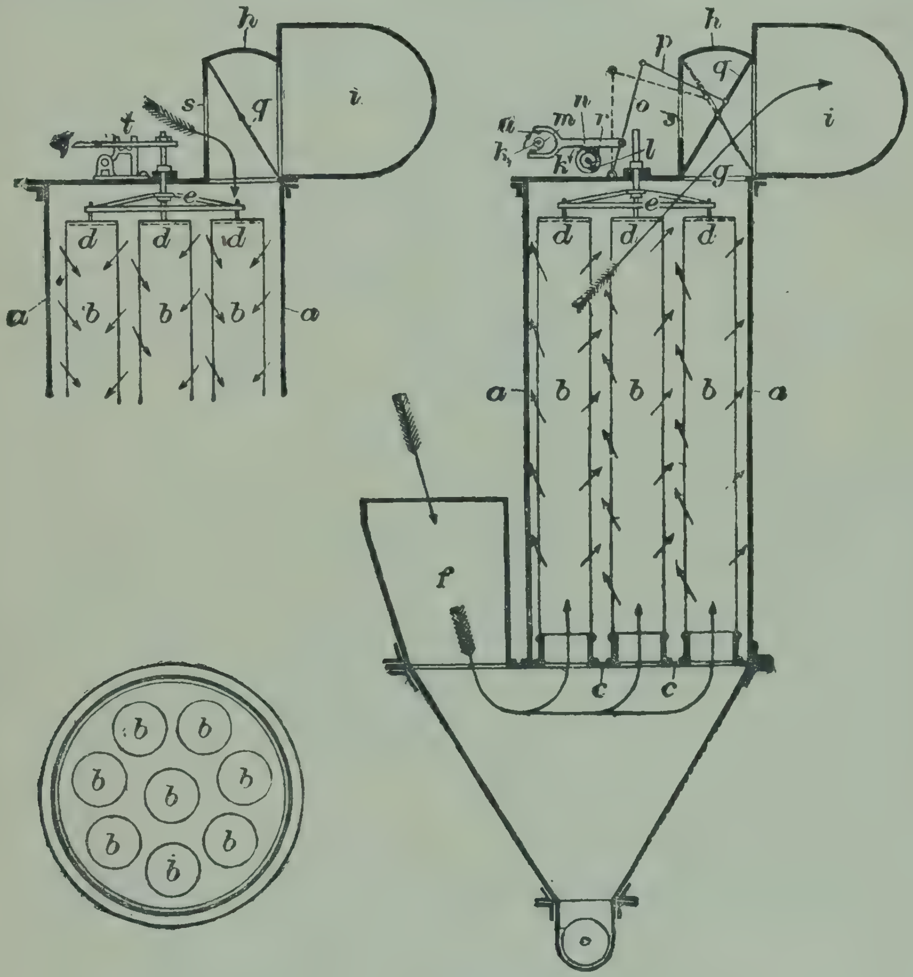


FIG. 22.—The Beth Dust Collector.

At the lower end of the cylinder is the **kiln hood**, which in modern plants is usually mounted on wheels, so that it can be run back when required, thus giving easy access to the interior of the kiln.

The hood is usually made of steel plate lined with fire-brick, and is provided with a door, two or three sight holes, and the burning attachments.

The **fuel** used in modern practice is almost always fine bituminous coal dust or oil, though natural gas and producer gas are used to some extent. The coal must be thoroughly dried and very finely ground so that it only leaves a residue of about 5 per cent. on a sieve containing 180 meshes to the linear inch.

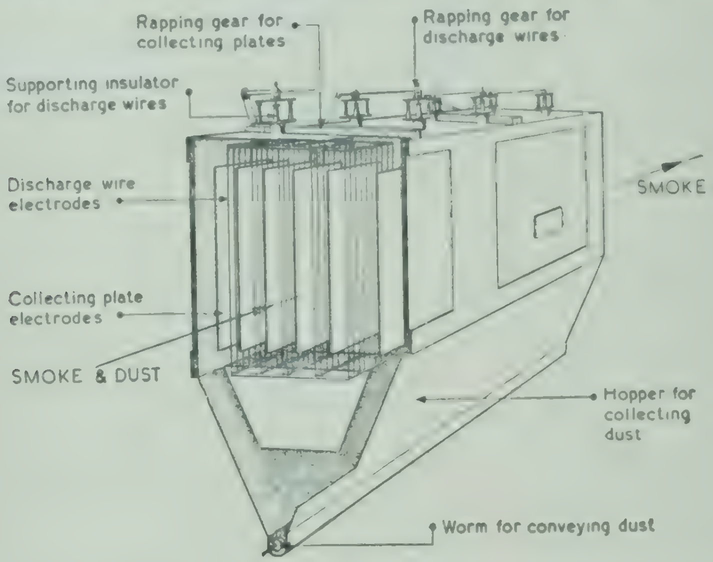

Rapping gear for collecting plates
Rapping gear for discharge wires
Supporting insulator for discharge wires
Discharge wire electrodes
SMOKE
Collecting plate electrodes
SMOKE & DUST
Hopper for collecting dust
Worm for conveying dust

FIG. 23.—Electrostatic Dust Precipitator. (*Cement and Concrete Association*)

As this finely divided coal is very explosive, great care has to be taken in handling. It is not usually stored, but is used as soon as it has been ground. When an initial crushing is required before drying this is usually carried out in hedgehog rolls (see p. 94), but sometimes the swing jaw crusher (see p. 92) or crackers of the coffee-mill type (see p. 86) are employed. The coarsely powdered coal is then usually ground in a tube mill, through which hot air, taken from the kiln, is passing. This serves the dual purpose of drying the coal and conveying it, when sufficiently ground, to the hopper feed of the kiln. The general arrangement is clear from the line diagram showing the kiln and accessories (Fig. 20). The finely divided coal from the mill is removed from the air stream by means of a cyclone precipitator and falls to the bottom of the hopper, where it is conveyed by a variable speed screw conveyor to the dust burner. The hot air from the cyclone is delivered by a fan into the burner and forms the primary air supply. A simple type of pulverised coal burner is generally used, that illustrated in Fig. 24 being typical.

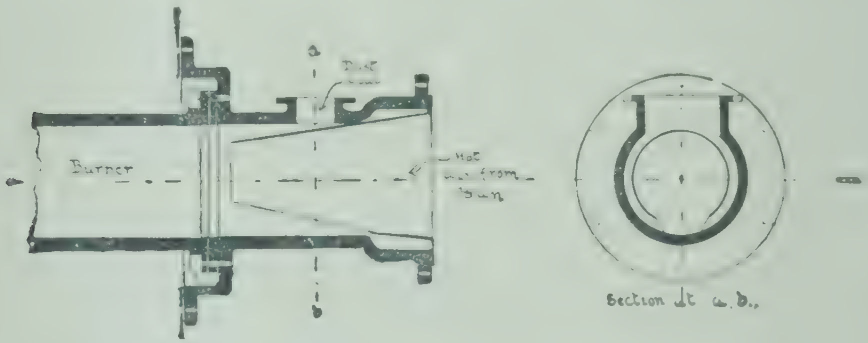


FIG. 24.—Coal Dust Burner Attachment.

The greater portion of the air required for the combustion is conveyed into the kiln through the coolers by way of the clinker discharge chute. When the kiln is started the coal dust is ignited, and the temperature of the lower end of the cylinder is raised to white heat. As the raw material gradually descends the kiln it first gives up any water which may be present; when about half-way down it evolves carbon dioxide, then becomes heated to the clinkering temperature and forms into little balls, when it reaches the lower third of the kiln, and is finally discharged through a chute at the lower end into the **cooler.**

In many European plants the cooler is an inclined rotating cylinder about 30–50 ft. in length, and 4–5 ft. in diameter, the interior of which is provided with a number of channel irons. As the cylinder rotates, the clinker is continually lifted up by these irons and caused to fall, thus being exposed to the current of air which passes through the cooler on its way to the kiln. The cooler thus serves the double purpose of cooling the clinker and heating the air supply of the kiln. The cooling cylinders are supported and rotated in a similar manner to the kiln. The **Smidth** cooler is horizontal, and is surrounded for half its length by a second cylinder. The hot clinker first passes through the inner tube, and then travels backwards through the annular space between the cylinders, after which it is discharged into a hopper. Vertical coolers are very popular in America. The older forms consist of a vertical tower, the interior of which is provided with conical surfaces. The hot clinker is discharged from the kiln into a pit, from which it is raised by means of an elevator to the top of the cooler, in descending which it is spread over the conical surfaces, and thus exposed to a current of cold air supplied through branches from a central blast-pipe. The clinker may also be partially cooled by sprinkling with water as it descends into the elevator boot. The whole of the heat given up by the clinker is lost when coolers of this type are used, but a portion of the heat may be utilised in some forms of the vertical cooler, such as the **Mosser** cooler shown in Fig. 25. The cold air enters through the central blast-pipe, and passing through holes arranged in rings at intervals of 5 ft. along the pipe, enters the inner cylinder, where it cools the clinker. The heated air then passes through holes in the wall of this cylinder into the outer one, from which it is conveyed to the coal feed. The holes in the blast-pipe and inner cylinder are protected by shields in the manner shown in the figure. In **shaking coolers** the hot clinker from the kiln falls into

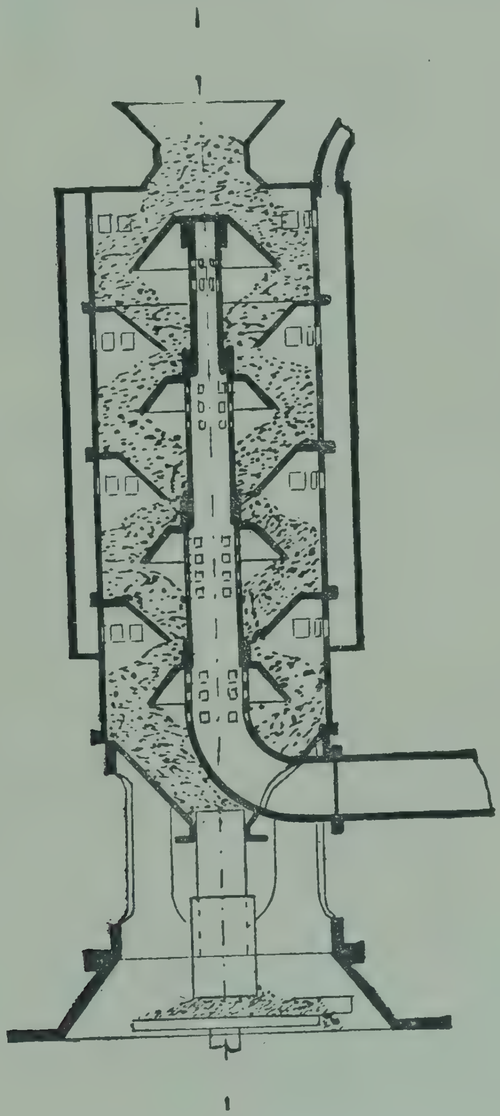


FIG. 25.—Mosser Vertical Cooler.

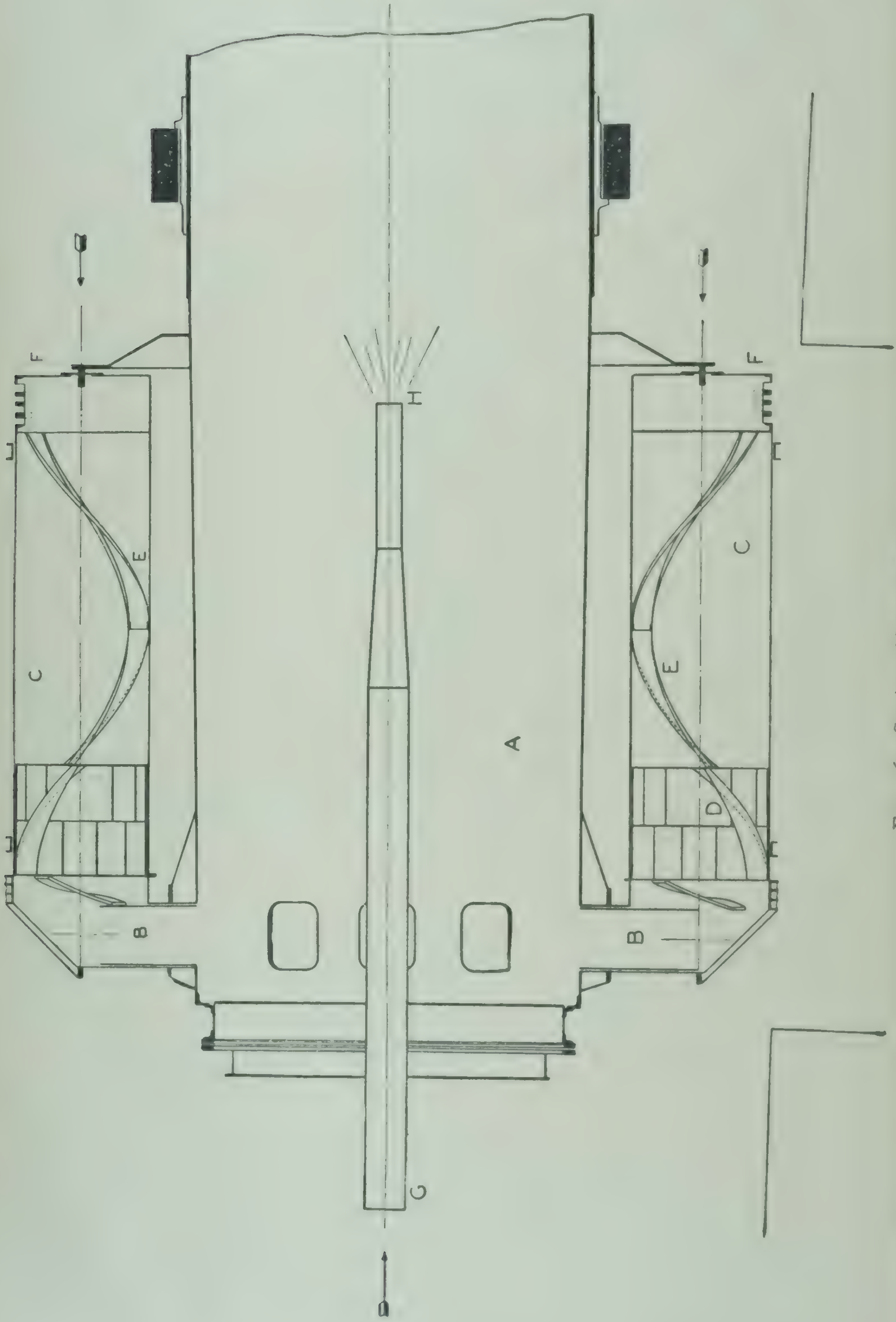


FIG. 26.—Section of Recuperator.

an enclosed inclined tray, the bottom of which is formed by a series of steps. The tray is kept in motion by means of cams carried on a revolving shaft, and the shaking motion thus imparted to the clinker gradually spreads it over the steps and carries it to the lower end, where it is discharged. Cold air is drawn in at both ends of the tray, and, after cooling, the clinker is discharged into the hot air chamber from which the kiln is supplied.

Recuperators

In very recent kilns, such as the one outlined in Fig. 20, the cooling of the clinker and the heating of the air for combustion are done in recuperator cylinders placed round the outer circumference of the lower end of the rotary kiln. The construction of such an apparatus, as in the Vickers-Armstrong "Reflex" kiln, is shown diagrammatically in Fig. 26.

The main body A of the recuperator is formed by the prolongation of the kiln shell. This section tapers towards its discharge end, thus retarding the rate of travel of the material, the high grade heat recovered from the material being returned directly into the burning zone of the kiln. The material where it is discharged by chutes B into the twelve or more auxiliary outer cylinders C is therefore reduced to a moderate temperature, and it is finally cooled and conveyed through the cylinders C by special cascaders and delivered at the point D. In order to remove the maximum amount of heat from the material in the main body A of the recuperator, lifters E are fitted of such a size as to turn the material over, and at the same time to maintain clear vision into the burning zone of the kiln. The main body A is lined with fire-bricks, thus reducing radiation losses to a minimum, and the chutes B have renewable liners. The feed end of each outer cylinder C, under the chute B, is lined with renewable plates, which, together with all lifters and liners in the main body A and chutes B, are of special heat-resisting metal. The cold air, entering the outer cylinders C at the end D, travels in the opposite direction to the flow of the material directly into the kiln, taking with it the heat recovered from the material.

THE LURGI CEMENT ROASTING PROCESS

In the years 1940–41 four plants were built in central Europe for the manufacture of Portland cement, not, as usual, in a rotary kiln, but on a travelling grate, the Lurgi sinter band. As compared with a rotary kiln, the new process presents many advantages.

The amount of steel required by the new plant is less than that of a rotary kiln, and the process is very flexible and economical as regards fuel, permitting the use of lean fuel, such as coke breeze or high-ash coal.

For small capacities, of from 100 to 200 tons/day, a circular type of sinter grate with very low capital cost can be used. For large capacities, of from 300 to 750 tons/day, a straight-line type is chosen, which for several decades past has proved itself very efficient in the field of sintering iron and non-iron ores in industrial practice. This is illustrated in Fig. 27.

The principle of the Lurgi cement burning process is shown in the diagrammatic layout (Fig. 28). As can be seen, one hopper contains dry mixed cement raw material, a second hopper fuel, *e.g.*, coke breeze of a size of 0–3 mm., and a third hopper sinter returns. To these three constituents water is added, and they are subsequently mixed and formed into granules in a mixing drum. The mixture is then charged in a layer, 6 ins. to 12 ins. thick, on to the sinter grate. It is ignited at its surface and sintered by drawing air through the charge. The fuel therefore burns in direct contact with the cement raw material. The clinker is discharged from the sinter grate and crushed in a grizzley before being classified on a screen into sizes of 0–7, 7–20, and above 20 mm. The fines, of less than 8 mm., are used as "sinter returns" and are returned to the mixture. The size of 7–20 mm. is fed in a layer of 1.5 ins. to 2.0 ins. depth directly on to the sinter

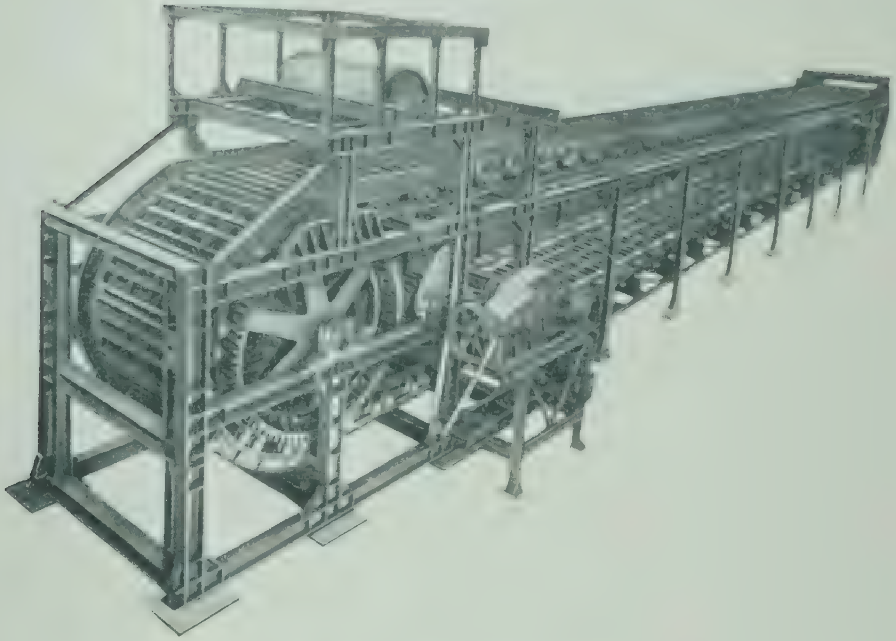


FIG. 27.—Lurgi Sinter Grate.

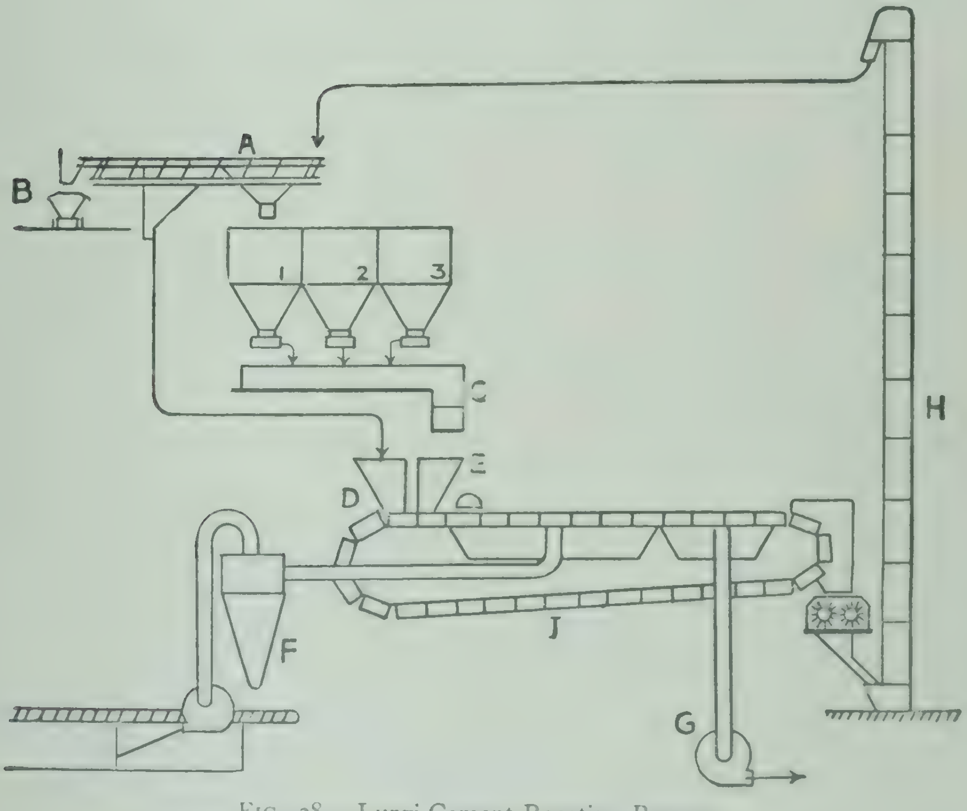


FIG. 28.—Lurgi Cement Roasting Process.

A. Sieving Machine.
B. Clinker Production.
C. Mixing and Granulation Chamber.
D. Returned Sinter 7–20 mm.
E. Mixing.
F. Cyclone.
G. Hot Gas Suction.
H. Elevator.
I. Sinter Grate.

Hopper 1—Sinter Returns.
2—Coke Breeze.
3—Cement Raw Material.

grate as a protective layer. The size of 7–20 mm., as well as the oversize (above 20 mm.), can be carried to the cement mill as finished product. By screening the precrushed clinker only, properly sintered material will be fed to the cement mill.

In the plants erected so far, the waste gases are drawn off by a fan at a temperature of from 150° C. to 170° C., but industrial practice has shown that one may advantageously draw off two gas currents, the main gas current with temperatures ranging from 80° C. to 100° C. goes to the stack, while a smaller gas current from the tail of the machine is drawn off at a temperature ranging from 300° C. to 350° C. The dry gases at a temperature of about 350° C. may be utilised for drying the raw material, particularly in a combined grinding and drying plant, which will enable a heat recovery of about 150 k.cal. The following summary shows the essential features of the Lurgi cement burning process, and the claims by Lurgi of performance and operational data.

1. **Heat consumption,** when using waste gases: 1,000–1,100 k.cal./kg. of clinker. This is about two-thirds the normal heat consumption of a rotary cement kiln.

2. **Quality of sinter band cement**: usually at least equal to rotary kiln cement.

3. **Dust content of waste gases**: The dust content of 0.8 gr./cu. m. is so low that no special dedusting plants are required (total dust losses at Oppeln, 0.5 per cent. on an average per year).

4. **Power required**: 20 kW./t. of clinker.

5. **Labour**: for medium capacities the labour required is about the same as that for rotary kilns; for larger capacities it is less.

6. **Repairs**: The sinter machine requires a minimum of repairs; there is a continuous replacement of grate bars, the cost of which is, however, considerably lower than that of the brickwork repairs periodically occurring in rotary kilns, which entail expensive stoppages.

7. **Capital cost**: The steel, material, and space required by a Lurgi cement sinter plant are considerably lower than those of a rotary kiln plant.

8. **Fuel required**: The fuel required in a size of 0–3 mm. and 0–4 mm. need neither be dried nor ground. In addition to coke breeze, lean fuel and waste fuel may be used, since no low temperature carbonisation products are involved.

9. **The daily output** of a single sinter machine may be as high as 750 t.

10. (*a*) The sintering can be carried through independently of the melting point of the mix, and it is possible to produce high alumina cement and special cements of all kinds irrespective of whether lime or anhydrite is taken as initial material.

(*b*) The plant need not operate continuously for 24 hours, but it may be operated for a period of 8–16 hours, and both started and shut down at will.

(*c*) No additional fuel or power is required for starting up and shutting down the plant.

11. **Control of operations**: The plant is simple and easy to supervise, the sintering process taking place under the eyes of the operators. By altering the quantity of fuel added the plant can be readily regulated at operator's wish.

STATIONARY OR VERTICAL KILNS

The old-fashioned **dome** or **bottle kiln** resembles the common lime-kiln, but has a conical chimney in order to increase the draught. It is quite obsolete, but there are several modifications still in use in some old works. In the **Johnson**

kiln (Patent No. 1,583, 1872), which is shown in Fig. 29, there is a long horizontal arched flue connecting the kiln, which is of the bottle shaped type, to the somewhat lofty cylindrical chimney. This flue is of the same width as the kiln, and is of sufficient length to hold enough wet slurry for the next charge.

The somewhat similar **Gibbons kiln** has two or more drying chambers which are used alternately; the hot gases pass both over and under the wet slurry, thus giving a larger heating surface. In the **Batchelor kiln** there are two arched chambers placed one above the other with flues beneath the lower tier. The hot gases from the kiln pass through the drying chambers and flues, thus drying the slurry from above and below, and are finally discharged through a chimney at the rear. In many cases one powerful shaft is made to serve several kilns. **Spackman's kiln** is designed for the use of slurry which is made into bricks. The kiln is of the ordinary form with a conical shaft, and a rectangular drying chamber is arranged alongside at a convenient level for loading. The mouth of the conical chimney is provided with a damper, which is closed when the combustion is nearly completed, whilst the dampers of the underground flues leading to a lofty chimney are raised. These flues pass under the drying chamber, and the hot gases enter the latter through holes in the floor, thus drying the contained bricks, the heat of the cooling kiln being quite sufficient for this purpose.

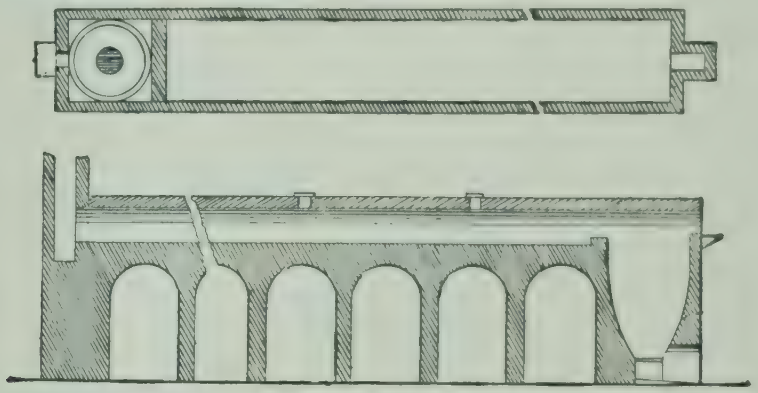


FIG. 29.—The Johnson Kiln.

The **Hoffman ring kiln** (described under **Brickmaking,** p. 235), was originally introduced for the burning of bricks, but it is also used for burning lime and Portland cement clinker.

This kiln is very economical in fuel, but expensive in labour. It is largely used on the Continent, but has not proved very successful in England.

Most of the **continuous stationary kilns** are very narrow in proportion to their height, and are therefore known as **shaft kilns**; they are also known as **stage kilns** (*Etageofen*), because they are sometimes divided into zones or stages. These kilns are better suited to the dry process of manufacture than the wet, the raw meal being made into briquettes which are dried in separate drying floors or tunnels. They are more common on the Continent than in this country. In some of the modern forms forced or induced draught is employed, as this leads to more rapid production and greater economy. In this case the chimney need not be so high as in the older types; there is, however, more risk of overburning and fusing the clinker.

A modern form of the **Dietzsch kiln** is shown in Fig. 30, which represents two kilns placed back to back, this being the usual arrangement.

The kiln consists of four zones or chambers placed one above the other and surmounted by the chimney shaft. At the top is the preheating zone A, into which the dry slurry in the form of half-bricks is introduced through the loading eye E, and gradually heated to redness by the hot gases as they pass from the lower part of the kiln on their way to the chimney. The preheating zone is inclined at its lower end towards the burning zone B, where the fuel is fed in through the doors F. The mixture of cement material and fuel is drawn down by means of rakes passed through openings in the shaft into the clinkering zone C, from which it passes into the cooling zone D, any masses which remain stuck to the walls being pushed down by means of iron tools thrust through the openings G. The burnt clinker in the cooling chamber is cooled by means of air entering the grate H, and is withdrawn at regular intervals, more raw material and fuel being added through E and F to take its place.

The fuel is usually small coal, which should be of good quality, the amount used being about 17–20 per cent. of the weight of the clinker produced. The output of the double kiln is from 20–30 tons per day.

The **Aalborg kiln**, shown in Fig. 31, is of Danish origin, and is now extensively used throughout the world. The clinkering zone is considerably constricted, and the cooling zone is conical in section with the larger diameter downwards. The raw material is fed in at A, and the fuel (coal) through a number of channels which slant downwards so as to enter the kiln below the clinkering zone. These firing holes are closed by means of iron covers when not in use. This kiln is very economical, the output is from 12–14 tons per day, and the coal consumption is only from 12–15 per cent. of the weight of burnt clinker. The "R" kiln is somewhat similar to the Aalborg, but there are two preheating chambers with a passage between, the floor of which is perforated for the introduction of the fuel (small coal): these holes are closed by covers when not in use. There are also openings in the walls of the shaft for assisting the descent of the clinker. The kilns are arranged in groups surrounded by a kiln house, which usually has four floors besides the ground floor. The top floor is the charging floor, the next is the firing floor, and the other two are for gaining access to the clinkering and cooling zones. The output of this kiln is 18 tons per day, and the coal consumption about 16 per cent. of the weight of clinker produced. The **Stein ribbed kiln** differs considerably from the shaft kilns already described. It consists of a cylinder from 6 ft. 6 in. to 8 ft. in diameter, and from 23–30 ft. in height, built up of cast-iron rings with channels on the outside. The cylinder is supported on short columns of masonry, and the top is covered by a conical iron hood furnished with four holes, which may be closed by means of doors for the purpose of charging. Above this hood is the chimney, which is provided with a damper at the top in order to regulate the draught. The kiln has a special form of basket grate which facilitates the operation of drawing the clinker. It is claimed for this kiln that, owing to the rapid cooling of the walls, the clinker shows no tendency to adhere to the sides. The output of a kiln of the largest size is about 15–16 tons per day.

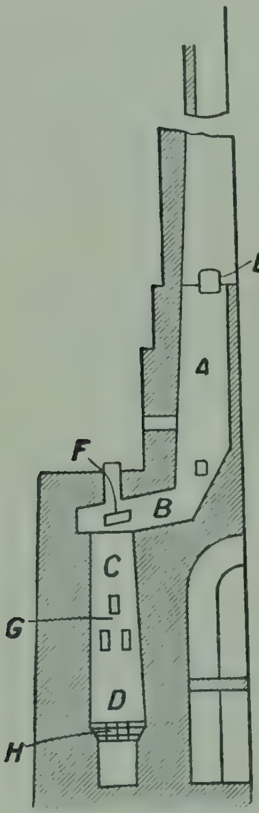


FIG. 30.—The Dietzsch Kiln.

Among other well-known kilns may be mentioned the **Schneider**, the **Hauenschild**, and the **Hotop kilns**, all of which possess some advantage.

Storing and Grinding the Clinker.—The clinker may be ground as soon as it is cool, or it may be stored for a time before grinding. In the case of **rotary**

clinker, storing for a period of about two to six weeks is sometimes resorted to in order to soften the clinker; the effect of this treatment depends, however, upon the degree of burning, and the composition of the clinker.

Low-limed clinkers readily fall to powder, and those which are higher in alumina crumble more readily than those which are more siliceous. The storing may also be carried out for the purpose of having a reserve of clinker upon which to draw when required, or for other reasons.

The clinker from **vertical kilns** always contains some under burnt and over-burnt material, the former being known according to its colour as **half-burnt, slack,** or **pink**. Under-burnt clinker is a comparatively soft material and generally has a greenish-grey colour, but is often yellow or pink, and may even possess a reddish or purple tint. Over-burnt clinker is a dense, hard, non-porous material with a metallic appearance, and is generally of a dull bluish black colour. Properly burnt clinker is a dark brown or greenish black, more or less porous substance, somewhat resembling coke in appearance. Before the clinker is ground it is necessary to pick out carefully all the under-burnt material, which is thrown aside to be reburnt. The over-burnt material should also be removed, but this is of less importance, as it is merely an inert substance, whilst the under-burnt clinker is actually harmful. The clinker from **rotary kilns** is in the form of small rounded lumps which are much harder, and usually much darker in colour,

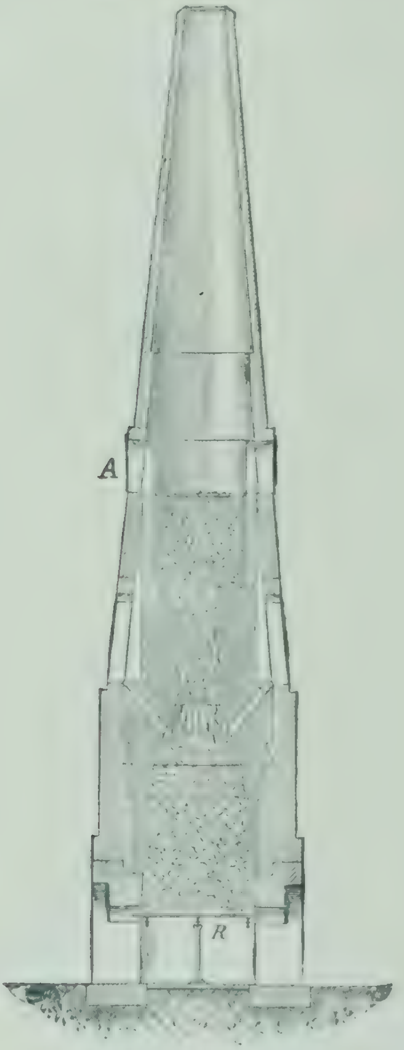


FIG. 31.—Aalborg Kiln.

than that produced in vertical kilns, and like the latter it usually contains some under-burnt and over-burnt material, though, as the kiln is under more complete control, these should only exist in comparatively small amounts.

It is usually necessary to add a little gypsum or plaster of Paris to the clinker in order to regulate the setting time. This is especially the case with **rotary clinker,** which sets almost instantaneously if it is ground as it comes from the coolers without any further treatment. The usual quantity of gypsum added is from 2–3 per cent. of the weight of the clinker. **The clinker from vertical mills** is first crushed to about the size of a hazel nut in a coarse crushing machine. The crushed material is then ground fine in the ball mill, followed by the tube mill.

In Germany a **sieveless ball mill** has been recently introduced, in which the finer particles are removed from the mill almost as soon as they have been produced by means of a **selector sifting machine.** The output of this mill is said to be about 20 per cent. higher than that of any other type for cement of standard fineness, or a superfine cement known as **selector cement** may be prepared at the same cost as ordinary Portland cement. This cement is, of course, in no way superior to any other Portland cement ground to the same degree of fineness.

Rotary clinker is usually small enough to go straight to the grinding mills without any previous crushing, and is therefore usually conveyed by means of shaking or tray conveyers from the cooler to an elevator, which delivers it to the hopper of the grinding mill or to the clinker store. It is, however, sometimes necessary to pass it through the crushing rolls in order to crush any large balls which it may contain, or these balls may be separated by means of a coarse sieve or grid placed at the end of the cooler. On account of its extreme hardness rotary clinker is more difficult to grind than that from vertical kilns. The tube mill is especially suitable as a finishing mill in the case of rotary clinker, as it offers a ready means of regulating the setting time by adding steam during grinding. This method, which is due to **Bamber**, consists in passing steam under a suitable pressure into the mill through the hollow trunnion at the feed end; the time of setting of the finished cement will depend upon the pressure of the steam admitted.

When edge-runners are employed for grinding the clinker the ground cement is conveyed from the mills to an elevator which raises it to the sieves, by which the coarser particles are retained and returned to the mills for further reduction, whilst the fine flour passes on and is conveyed to the warehouse, where it is deposited in bins or silos. The sieves used are of various kinds and shapes. Revolving sieves which are circular, hexagonal, or octagonal in cross section are often used, as are also flat shaking sieves. Air separators are often employed instead of sieves for separating the cement, and their use is rapidly increasing. The **air separator** is described under **Manures,** p. 28.

Storing and Packing.—The finished cement is conveyed by means of elevators and conveyers to the storage bins or silos, where it is usually kept for a few weeks before packing.

Some works in this country employ flat-bottomed bins, the floors of which are level with the loading platform, and the cement is dug out from these and packed by hand. In most modern works, silos with hopper-shaped bottoms are used, as shown in Fig. 32. The cement is discharged through a spout into sacks or barrels placed beneath, the packing often being done by means of automatic machines. In most American works the silos have slightly sloping floors, and automatically discharge their contents into a common tunnel. The cement is transmitted by means of a screw conveyer placed in the tunnel to the packing room, where it is elevated to a hopper beneath which the automatic filling machines are arranged. Portland cement is packed in sacks or barrels, shaking machines often being employed in order to ensure the cement being well shaken down.

Dust Collectors.—As might be expected, a large amount of dust is generated at most of the stages of the process of cement manufacture, and as this dust is not very objectionable, but represents a considerable financial loss, it is very advantageous to collect it by some means. Expansion chambers are the only means available for separating the dust from gases at a high temperature, as in the case of the air from the driers, kilns, and coolers. They may also be used for collecting the dust from the crushing and grinding mills, but filters and collectors depending upon centrifugal force are also employed. In the first case the air is usually drawn by means of a fan through one or more sheets of cloth held in light frames. Often, as in the case of the **Beth dust collector,** shown in Fig. 22, the filters are in the form of cylindrical sleeves, which are automatically cleaned.

Electrostatic precipitators are now becoming standardised in modern cement works. A typical unit is illustrated in Fig. 23.

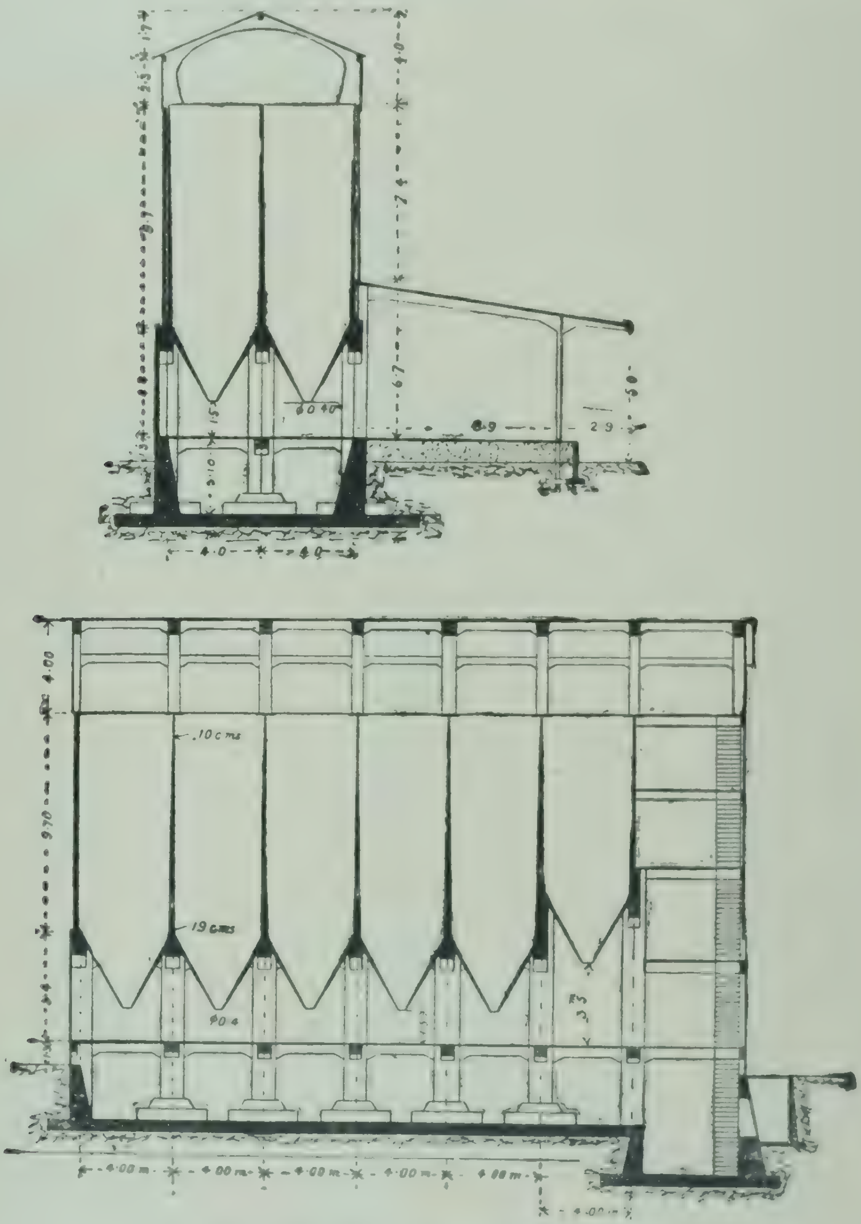


FIG. 32.—Silos with Hopper-Shapped Bottoms.

Weighing Machines.—The use of weighing machines at various stages of the manufacture of cement is indispensable in modern practice. These are often of the steelyard type, such as the ordinary platform weighing machine, or the hopper weighing machine in which the material is fed into the hopper until the required load is obtained, when it is discharged by means of a lever which operates on the door in the bottom of the hopper. In most cases, however, automatic weighers are to be recommended. **Avery's automatic hopper weigher** is much used. The **rotating weigher** and the **Blake Denison automatic weighers** are also good machines.

Automatic weighing machines are also employed for weighing the material into sacks or barrels. In **Simon's dustless sack filler and weighing machine** the sack is attached to a trunk which is suspended from one arm of the balance beam, whilst the weights are suspended from the other.

On working a lever the filling operation commences, and as soon as the sack contains the required amount the supply is automatically cut off. Four bags per minute can be filled with this machine. An automatic cask-filling machine is also on the market.

Composition of Portland Cement.—Although, as stated on p. 88, Portland cement may be made from a great variety of raw materials, the composition of the finished product is practically constant. The essential constituents are lime, alumina, and silica; less important components are magnesia, oxide of iron, and the alkalis, whilst sulphur is usually found in small quantities, being either derived from the raw materials or the fuel, or added intentionally in the form of gypsum or plaster of Paris. Carbon dioxide and water do not exist in any notable quantity, except in old or improperly burnt samples. It is usually stated that there should be no free lime present, or the cement will "blow" and disintegrate after setting. B.S. 12, 1947, requires Portland cement to conform to the following chemical composition.

The ratio by weight of lime (less that necessary to combine with the sulphuric anhydride present) to silica, alumina, and iron oxide should not be greater than 1.02, nor less than 0.66, when calculated according to the formula:

$$\frac{CaO}{2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3}$$

The ratio of the weight of alumina to that of iron oxide should not be less than 0.66; the weight of insoluble residue, as determined on page 128, should not be more than 1.0 per cent.; that of magnesia should not exceed 4.0 per cent.; and the sulphur content, calculated as SO_3, should not exceed 2.75 per cent. The total loss on ignition should not exceed 3 per cent. for temperate climates or 4 per cent. for hot climates.

Magnesia is nearly always present in small amounts, being derived from the raw materials. Free magnesia behaves in a similar manner to free lime, but slakes much more slowly, the time taken being proportional to the temperature to which the material has been exposed in the kiln. Magnesia combines with silica and alumina to form silicates and aluminates similar to the corresponding calcium compounds, but which become hydrated much more slowly, so that a cement consisting of a mixture of calcium and magnesium silicates and aluminates is likely to suffer disruption after setting. According to Lea[1] and others the silicates and aluminates of magnesium possess no hydraulic properties, and magnesia is incapable of replacing lime in cement mixtures. The British Standard Specification (1947) does not permit more than 4 per cent. of magnesia in Portland cement.

Portland cement owes its colour to the **oxides of iron** which it contains. At the clinkering temperature these combine with the lime to form **ferrites** which, according to **Le Chatelier,** slake and decompose in the presence of water, but do not set. If any calcium sulphide should be present in the cement, this reacts with the iron compounds with the formation of ferrous sulphide, which is afterwards oxidised to ferric oxide.

The only **alkalis** usually found in Portland cement are **soda** and **potash**, which are mainly derived from the clays and clay shales. They are usually present to the extent of about 0.5–1 per cent. in the form of silicates, some of which are soluble in water, and may therefore play an important part as carriers of silicic acid during the setting of cement.

The **sulphur** in Portland cement is derived partly from the calcium sulphate and iron pyrites (iron sulphide, FeS_2) present in the clay and clay shales, and partly from the fuel. In addition to this sulphur, a small amount of calcium sulphate, in the form of plaster of Paris or gypsum, is frequently added after calcination. The British Standard Specification (1947) allows a maximum of 2.75 per cent. of sulphur trioxide (sulphuric anhydride, SO_3), and the German "Normen" fixes the limit at 2.5 per cent. The action of these small amounts of added calcium sulphate is beneficial, as it retards the setting of the cement, which would otherwise be too rapid. In larger amounts it is injurious, partly because it is a much softer substance than cement, and partly because it is liable to be washed out of the mortar on account of its comparative solubility in water. The presence of sulphur in the raw materials is always objectionable, because it leads to the formation of calcium sulpho-aluminate, which is highly expansive, and also because of its tendency to become reduced to sulphide in the kiln. Thus, calcium sulphate is liable to become reduced to calcium sulphide, which then decomposes the iron compounds with the formation of iron sulphide.

---

[1] F. M. Lea, "Cement and Concrete," Lecture to R.I.C., 1945.

The following are typical analyses of Portland cement:—

	No. 1.	No. 2.	No. 3.
Lime	62.50	61.92	61.07
Silica	24.00	20.94	21.74
Alumina	6.10	7.56	8.01
Ferric oxide	2.44	5.02	4.35
Magnesia	1.16	1.20	1.04
Alkalis	0.41	0.91	0.83
Sulphuric anhydride	1.40	0.92	0.94
Water and carbon	1.55	0.95	0.81
Dioxide	...	...	...
Insoluble residue	0.44	0.64	1.08
	100.00	100.06	99.88

The properties of Portland cement do not, however, depend so much on the proportions of the constituents mentioned above as on their state of combination, and a great deal of work has been done on the composition of cement clinker and the process of setting and hardening. At the clinkering temperature lime combines with silica, alumina, and oxide of iron to form calcium silicates, aluminates, and perhaps alumino-silicates, such as—

Tricalcium silicate	$3CaO.SiO_2$.
Tricalcium aluminate	$3CaO.Al_2O_3$.
Tetracalcium alumino ferrite	$4CaO.Al_2O_3.Fe_2O_3$.
Dicalcium silicate	$2CaO.SiO_2$.
Dicalcium aluminate	$2CaO.Al_2O_3$.
Monocalcium silicate	$CaO.SiO_2$.
Monocalcium aluminate	$CaO.Al_2O_3$.

The first four of the above compounds are present in Portland cement; mono-calcium aluminate is present in high alumina cements, whilst mono-calcium silicate is present in blast furnace slag. According to **Le Chatelier**,[1] who was one of the earliest investigators in this field, tricalcium silicate is the constituent to which the hardening of Portland cement is due. It cannot be formed by the direct combination of lime and silica, but is produced in the cement clinker by the fusion of lime and silicate.

According to Lea (*loc. cit.*), from considerations of equilibrium diagrams for the ternary systems $CaO-Al_2O_3-SiO_2$, and $CaO-Al_2O_3-Fe_2O_3$, some typical calculated compounds present in Portland cements, on the assumption of complete equilibrium, are shown in the following table:—

TYPICAL CALCULATED PERCENTAGE COMPOUNDS OF PORTLAND CEMENTS (Lea)

Compound.	Rapid Hardening.	Normal.	Low Heat.
$3CaO.SiO_2$	40–65	30–50	10–35
$2CaO.SiO_2$	3–35	20–45	40–60
$3CaO.Al_2O_3$	7–15	7–15	3–8
$4CaO.Al_2O_3Fe_2O_3$	5–12	5–12	5–15
MgO	1–4	1–4	1–4
Uncombined CaO	0–4	0–3	0–1

The examination of polished surfaces and sections of cement clinker under the microscope reveals a number of crystalline components which have been given names, by analogy with those employed in metallurgy, by various investigators, particularly Le Chatelier (*loc. cit.*) and Törnebohm. These are discussed in some detail on p. 126.

---

[1] Le Chatelier, *Compt. rend.*, 1882, 94, 867; 1883, 96, 1056; *Annales des Mines*, 1887 (8), 11, 345; "Sur la Constitution des Mortiers Hydrauliques," 1904.

High Alumina Cement (Ciment Fondu)

This is formed from chalk and bauxite. These are ground and mixed together in the dry state, after which they are heated in reverberatory furnaces till fused. The molten material is cast into pigs, which are crushed in tube mills, without the addition of any extraneous material. Because of the great hardness of the fused mass, grinding costs are greater than with Portland cement.

Typical compositions are:

	Per cent.	Per cent.
SiO_2 - - -	5.1	5.6
Al_2O_3 - - -	39.0	36.7
Fe_2O_3 - - -	12.9	11.6
FeO - - -	4.1	5.1
TiO_2 - - -	1.6	2.1
CaO - - -	37.3	38.9

The ratio of $\frac{\%Al_2O_3}{\%CaO}$ should not vary outside the limits 0.85 and 1.3. The principal compound present in ciment fondu is mono-calcium-aluminate (Al_2O_3CaO).

There are five major chemical constituents in high alumina cements, namely CaO, Al_2O_3, SiO_2, Fe_2O_3, and FeO. Minor constituents are TiO_2 and MgO. The examination of polished and etched surfaces reveals the following compounds, in addition to the major constituent mono-calcium aluminate, in the form of long dendrites or prisms, set in a background of ferrite and ferrous iron containing material: $5CaO.3Al_2O_3$; $2CaO.Al_2O_3.SiO_2$; $2CaO.SiO_2$; $4CaO.Al_2O_3.Fe_2O_3$; and $CaO.TiO_2$.

The Hydration of Cements

The following is a summary of a recent paper by Lea (*loc. cit.*) on the composition and mode of hydration of Portland cement:—

"The setting of cements with water is now considered due to the formation of supersaturated solutions which subsequently precipitate as hydrated compounds, and are relatively insoluble in water. Inorganic compounds that do not possess this property do not form good cements, whilst even within systems containing CaO, SiO_2, Al_2O_3, and Fe_2O_3 the range of composition of good cements is small, and the setting properties are influenced markedly by such factors as fineness of grinding, and the presence of small proportions of other inorganic salts, such as, for example, calcium sulphate or calcium chloride. When tricalcium silicate reacts with water, a supersaturated solution is formed, which rapidly precipitates a less basic hydrated calcium silicate and accumulates lime in solution until the saturation point is reached, when calcium hydroxide is also deposited. With dicalcium silicate, the initial supersaturated solution has a CaO : SiO_2 molar ratio of 2 : 1 and a hydrated silicate is deposited. In the presence of excess water, calcium hydroxide crystals also form slowly, but in pastes of limited water content only traces appear, even after many months. It appears, therefore, that the lime concentration required to stabilise the hydrated dicalcium silicate is very close to that of a saturated lime solution, and there is still some doubt whether the hydrated silicate formed in the setting of both $3CaO.SiO_2$ and $2CaO.SiO_2$ in Portland cement is $2CaO.SiO_2.aq.$ or $3CaO.2SiO_2.aq.$, the remaining lime appearing as $Ca(OH)_2$.

The hydration of tricalcium aluminate presents a more complex picture. In water it gives rise to a supersaturated solution from which either the hexagonal or the cubic form of hydrated tricalcium aluminate is precipitated, whilst in saturated lime water the hydrated tetracalcium aluminate results. When gypsum is present, calcium sulpho-aluminate is formed. The reaction with water is very rapid and is accompanied by a considerable heat evolution and an almost immediate set, but when sufficient gypsum is present there is little heat evolution and no flash set. The iron compound $4CaO.Al_2O_3.Fe_2O_3$, hydrates rapidly in water, like $3CaO.Al_2O_3$, but setting is delayed for a few minutes, and there is no comparable heat evolution. The presence of gypsum retards the set and probably results in the formation of a calcium sulpho-ferrite, whereas in water the products of hydration are hydrated tricalcium aluminate, either in the hexagonal or cubic form, and, perhaps, hydrated monocalcium ferrite. The latter remains in some doubt, since Schläpfer states that free calcium hydroxide is also formed. There may also be some solid solution of $3CaO.Fe_2O_3.6H_2O$ in the cubic form of hydrated tricalcium aluminate and this would lead to the formation of a corresponding amount of hydrated ferric oxide.

The composition of the initial solution, established when cement is brought into contact with water, depends more on the rate at which the various compounds present react with water than on their relative proportions. Thus, minor constituents of the cement, such as the gypsum added to control its set, and part of the alkalis present in the cement clinker, pass into solution very rapidly and, even though the proportion present in the cement is small, they can, in the limited amount of water present, establish relatively high initial solution concentrations and thus exercise a marked influence on the liquid environment in which the hydration of the main cement compounds proceeds.

It has been shown by Forsen that when silica and alumina accumulate in solution they interact to precipitate a gel containing hydrated alumina and silica, together with lime. The formation of this gel leads to a quick set and, in addition, the resultant coating of the tricalcium silicate grains retards their further hydration and, consequently, the development of strength. The primary effect on the setting process of other ions which may be introduced into this solution is exercised through their influence on the concentration of alumina in solution. In order to obtain normal setting and uninhabited development of strength, it is necessary that the concentration of alumina in solution be kept very low so that the silicates can hydrate to form the hydrated calcium silicate bonding agent. This is the function of the gypsum which, added to cement to the extent of a few per cent., controls the setting time by precipitating the alumina as calcium sulpho-aluminate.

Essentially, retarders of set, which include other materials than gypsum, are compounds which precipitate the aluminate from solution, whilst quick setting occurs when no retarding agent is present, or when the aluminate solubility is increased by the presence of other agents.

All the calcium aluminates that occur in cements, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$, and $5CaO.3Al_2O_3$, react with water to form supersaturated solutions, and a similar behaviour is observed with high alumina cement itself. In the presence of excess water, hydrated alumina and $2CaO.Al_2O_3.8H_2O$ are deposited.

One important factor determining the rate of setting of high alumina cement is the extent to which crystallisation has occurred during cooling of the clinker. Cements containing an excessive proportion of uncrystallised glass tend to set very slowly, while cements that are entirely crystalline tend to become very rapid setting. The setting time of high alumina cement is therefore controlled in considerable measure by the rate of cooling of the molten material in the moulds and no addition, such as that of gypsum to Portland cement, is made. The composition of the cement is also important in relation to setting time, which tends to become faster, for instance, as the $CaO : Al_2O_3$ ratio increases.

Whereas, when Portland cement sets, lime is liberated, when high alumina cement sets, excess alumina is precipitated as a gel. Consequently, high alumina cement is more stable to attack by mineral sulphates, such as those of calcium, magnesium, and sodium, provided the pH is greater than 3.5-4.0, which is the point at which alumina gel commences to redissolve in acids."

Heat of Hydration of Cements

The heat of hydration of cements plays an important part in their behaviour during setting. Thus, high alumina cement, which evolves 70–80 calories per gram during the first 24 hours of mixing with water, enables the cement to be mixed during frosty weather, whereas the gradual evolution of heat with normal cements in massive structures, such as dams, may cause failure of the structures due to unrelieved stresses. Lea and Desch[1] have published the following table for the heat evolved during hydration of the compounds present in Portland cement when ground to the normal fineness.

HEAT EVOLVED ON HYDRATION—CALORIES PER GRAM
(Lea and Desch)

Compound.	Time after mixing with water.			
	3 days.	7 days.	28 days.	180 days.
$3CaO.Al_2O_3$ - -	170	190	200	220
$3CaO.SiO_2$ - -	100	110	115	120
$4CaO.Al_2O_3.Fe_2O_3$	30	45	50	75
$\beta 2CaO.SiO_2$ -	20	20	45	55

From these data Lea (*loc. cit.*) has deduced the basis on which the required composition of a Portland cement of "low heat" evolution can be formulated. The compounds, $3CaO.Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$, do not contribute greatly to the strength of the cement, but the presence of some alumina and ferric oxide is necessary in manufacture to reduce the temperature of burning of the clinker, and to facilitate combination of the lime and silica. Hence, for a "low heat" cement, the first step is to reduce the alumina content and to raise the ferric oxide content, if necessary, thus resulting in the substitution of $4CaO.Al_2O_3.Fe_2O_3$ for $3CaO.Al_2O_3$. It is also necessary to reduce the lime content in relation to the acidic oxides in order partially to substitute $2CaO.SiO_2$ for $3CaO.SiO_2$. This last step causes a reduction in the rate of strength development, but not in the ultimate strength achieved. The above description is somewhat simplified, in that no account is taken of glass formation in the clinker. The comparative compound contents of normal and low heat Portland cements have been shown in the table on p. 116, and the comparative rates of heat evolution are given in the table below.

AVERAGE HEAT EVOLUTION OF CEMENTS
(Lea)

Type of Cement.	Heat Evolution: cals./gram.			
	3 days.	7 days.	28 days.	90 days.
Rapid Hardening Portland	90	100	110	115
Normal Portland - -	75	85	90	95
Low Heat Portland - -	45	55	65	75

Adulteration of Portland Cement.—The adulteration of Portland cement was at one time somewhat extensively practised. The choice of adulterants was limited, as only very cheap substances, which resembled Portland cement in colour and general appearance, could be used; the most usual materials employed for this purpose were **Kentish rag** (a siliceous limestone) and **blast furnace slag**, but other limestones, sandstones, old fire-bricks, etc., were also used. Such adulteration is rare at the present time, at least so far as British and German cements are concerned, and the most serious fraud is the substitution of cheap Belgium natural cements, or slag cements, for Portland cement.

Action of Sea Water on Portland Cement.—Sea water has sometimes been found to have a deleterious action on Portland cement. This was early attributed to the dissolving out of some of the lime from the cement, and the precipitation of salts of magnesium, and later on was considered to be due to the formation of sulpho-aluminates.

---

[1] F. M. Lea and C. H. Desch, "Chemistry of Cement and Concrete." London, 1935.

Portland cement is also liable to attack by waters containing sulphates in solution and this is again attributable to the formation of sulpho-aluminate by interaction with calcium hydroxide and hydrated calcium aluminates. Cements made from clinker that has been chilled rapidly so that most of the alumina is present as a glass, rather than as crystalline compounds, have an increased resistance to sulphate attack.

Types of Portland Cement

The three main types of Portland cement recognised in England, namely "Rapid Hardening," "Normal," and "Low Heat," have already been mentioned. In America[1] five main types are recognised, viz.:—

Type I (ordinary). For general use where types II to V are not required.
Type II. **Moderate Heat of Hardening Cement** for use in general concrete work exposed to moderate sulphate action, or where moderate heat of hydration is required.
Type III. **High Early Strength Cement** for use where high early strength is required.
Type IV. **Low Heat Cement** for use when a low heat of hydration is required.
Type V. **Sulphate Resisting Cement** for use when high sulphate resistance is required.

These types are all obtained by small changes in chemical composition and fineness of grinding.

Iron-Ore Cement. Many attempts have been made to prepare a Portland cement in which ferric oxide entirely replaces the alumina, but so far without success. Cements in which a large portion of the alumina is replaced by ferric oxide are, however, made.

In 1901 **Krupp** introduced a cement under the name of "**sidero cement,**" in the manufacture of which iron ores are wholly or partially substituted for the clay usually employed. The cements of this class are called **iron-ore cements**, and must be distinguished from the **iron Portland cements** (see p. 85). They are employed in marine work on account of their supposed resistance to the action of sea water. These cements contain a large proportion of iron, as is shown by the following analysis, which is due to **Michaēlis**:—

Analysis of an Iron-Ore Cement (Michaëlis).

Silica	23.26	per cent.
Alumina	1.67	,,
Ferric oxide	8.20	,,
Lime	64.84	,,
Magnesia	0.66	,,
Sulphur trioxide	1.08	,,
	99.71	per cent.

They are slow setting, and have a specific gravity of about 3.25-3.44

White Portland Cement.—There has been placed on the market a Portland cement which complies with the requirements of the British Standard Specification (1947), but which, owing to the absence of iron compounds, is white in colour. It was originally introduced in America, but is now used to some extent in this country.

It is very expensive and is therefore unsuitable for ordinary building purposes, but finds many useful applications, among which may be mentioned cement plaster or stucco, repairing and joining marble pillars and blocks, the manufacture of tiles and mosaic work. For the latter purpose the cement may be coloured by means of venetian red, yellow ochre, and many other mineral colouring matters.

Super-Cement.—This cement was originally intended to be a waterproof Portland cement, that is to say, an ordinary Portland cement to which material was added in order to render it waterproof. It has been shown, however, that the treated cement not only makes a waterproof mortar, but that the latter is much stronger than that made with ordinary Portland cement. The increase in strength is especially marked in the case of cement and sand mortar, and the difference increases with time.

The author has carried out a number of tests with this material, and has found the tensile strength after ninety days of a mortar made with one part of treated cement to three parts of standard sand to be about 50 per cent. greater than that of a similar mortar made with the same, but untreated, Portland cement. Other tests, carried out elsewhere, have shown that after six months the tensile strength of the mortar made with the treated cement and sand is at least double that of a similar mortar made with untreated cement. It is said to be ordinary Portland cement clinker ground with gypsum and tannic acid.

---

[1] R. H. Bogue, "The Chemistry of Portland Cement." New York, 1947.

Sand Cement.—This is only Portland cement diluted with sand. It is prepared by mixing together equal weights of Portland cement and sand, and finely grinding the mixture.

THE PLASTER CEMENTS

The plaster cements are prepared from **gypsum**, or the hydrated calcium sulphate, $CaSO_4,2H_2O$, by driving off all or part of the water of hydration, and therefore consist essentially of more or less dehydrated calcium sulphate.

The occurrence, properties, processes of mining, and the chemistry of **gypsum** have been fully discussed in a separate article by James Shelton, Vol. I., p. 345.

In the following pages, therefore, we confine ourselves to the description of the processes employed in the manufacture of the various cements which have gypsum as their basis.

If fairly pure gypsum be heated to a temperature of about 100°-200° C. it becomes partially dehydrated, yielding a sulphate of the composition $2(CaSO_4),H_2O$, which is known as **plaster of Paris**. If the gypsum be heated much above 200° C. it loses all its water, yielding the anhydrous sulphate $CaSO_4$. It is then said to be "**dead-burnt**," and is useless for plaster of Paris, as it has lost the power of readily combining with water. If, however, such over-burnt plaster be very finely ground, hydration will take place, although very slowly, and when prepared under certain conditions it is employed under the names of **flooring plasters** and **hard-finish plasters**. When gypsum containing a large amount of impurities is heated to between 100° and 200° C. the product resembles plaster of Paris, but sets much more slowly, and the same result may be obtained by adding certain materials to plaster of Paris after burning. These slow-setting impure plasters are known as **cement plasters**, although they are quite different from the plasters made from the hydraulic cements, which are also known as "cement plasters" (see p. 82). From what has been said above it will be seen that the plaster cements may be classified as follows :—

Plaster of Paris Cement plasters	Prepared at temperatures below 200° C.
Flooring plasters Hard-finish plasters	Prepared at temperatures considerably above 200° C.

Plaster of Paris and the Cement Plasters.—The processes of manufacture of these plasters are so similar that they may be treated together, the only difference being that a pure gypsum is employed for the manufacture of plaster of Paris, whilst the cement plasters are prepared either from impure materials, or by adding a retarder during or after manufacture. Only two operations are necessary, calcination and grinding, and the latter may either follow or precede the former, according to the method of calcination employed. In Europe it is usual to calcine first, but in America, where the "kettle process" is employed, the opposite is the case, though the European plan is followed where rotary calciners are used. Great care has to be taken that the temperature does not rise too high or fall too low, and also that the material does not come in contact with the fuel, as this would lead to the formation of calcium sulphide.

Calcining in Kilns.—The oldest and simplest method of preparing the plaster is to burn the stone in a kind of shed enclosed on three sides by brick or stone walls, and covered with a rough tiled roof. The large pieces of gypsum are arranged on the floor so as to form a series of rough arches parallel to the main walls of the shed ; and the remainder of the stone is placed on these arches, the larger pieces at the bottom, and the size gradually decreasing until at the top there are only dust and sweepings. Wood fires are then lighted in the arches ; the hot gases rising through the interstices between the stones gradually heat the mass, driving off the water of hydration, and finally escape through openings in the roof and upper parts of the walls. Sometimes coal is used as fuel, in which case the floor of the kiln is hollow, and the fires are lighted in these spaces, the flames passing into the kiln through holes left in the rooves of the arches. This crude kiln or shed is still employed on the Continent, but it is very wasteful, and the product is never uniform, as the lower layers receive more heat than the upper ones.

In the neighbourhood of Paris a kiln is employed which somewhat resembles the common lime-kiln (see p. 79), but has a cavity beneath the floor which serves as a fireplace. The flames and heat pass through openings in the floor into the kiln.

The **Dumesnil kiln**, shown in Fig. 33, is a great improvement on older kilns, as the heat is much more under control, and is evenly distributed over the whole mass of plaster-stone.

This kiln is circular in plan, and has an arched roof LL, in which are four small flues OO, and one large central one P, all of which can be closed by means of dampers. At the bottom of the kiln there is a central furnace D, the flames of which pass through flues EE into the fire-chamber G, and hence through twelve openings FF into twelve radiating arched flues MM built of the largest pieces of plaster-stone. There is a door at the side of the kiln for the purpose of emptying and unloading, and an opening N in the roof which serves for filling the top of the kiln. In working the kiln, the charge is calcined by means of a moderate fire; and then about 6 or 7 cub. yds. of unburnt stone are added at the top, and all the openings are closed, when the second lot of stone is dehydrated by the heat still contained in the first charge.

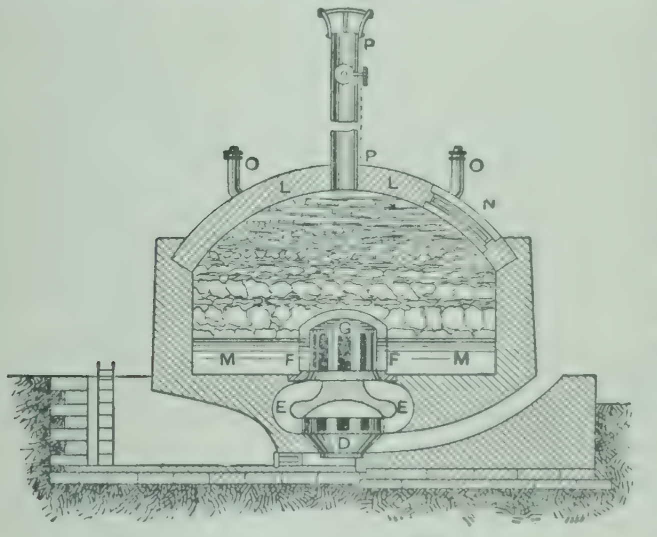


FIG. 33.—Dumesnil Kiln.

Although this kiln is expensive to build it is economical in working. Sometimes the plaster-stone is dehydrated by means of the waste gases from coke ovens. For this purpose the kilns and ovens are arranged thus.

The hot gases from ordinary coke ovens pass first into a flue, and then into a second flue, which leads to the kilns through holes in the floors of the latter. The hot gases may be shut off from any of the kilns by means of dampers. The water-vapour and gases finally escape from the kilns through the chimney F.

Superheated steam has also been employed for dehydrating gypsum.

A jet of steam, at a temperature of about 200° C., is blown alternately into each of two chambers charged with the raw material, when the water of hydration is rapidly absorbed by the steam, leaving the plaster ready for grinding.

It is a common practice in this country to prepare the plaster by a continuous method in a kiln resembling a baker's oven, in which the stone does not come in contact with the fuel, but is dehydrated by means of hot gases which pass from a furnace through a flue passing round and round the oven.

Best plaster is sometimes prepared on a small scale by the moulders by a process known as **boiling**. They first grind the raw stone to a fine powder and then spread the latter in a layer, about 2 or 3 in. in depth, upon a metal plate or shallow dish placed over a fire, care being taken to avoid too high a temperature. The water vapour given off from the lower layer appears to raise the remainder of the material and keep it in suspension with a peculiar motion to which the process owes its name of "boiling," and small craters are soon formed from which the steam escapes. The mass is stirred from time to time until no more water is given off, when the plaster is ready for use.

Rotary kilns for calcining plaster-stone have been in use for a number of years both in Europe and America. The process is a continuous one. In the **Mannheim calciner** there is a fire box placed in front of a chamber containing a rotating cylinder, the interior of which is furnished with shelves or buckets. Above the cylinder, and connected to it by a pipe, is the **forewarmer**, which consists of a chamber through which a worm conveyer passes from one end to the other. The crude gypsum is first crushed, but not finely ground, and is then conveyed by means of a bucket elevator to a bin placed above the calciner from which it descends into the forewarmer, where it is carried along by the worm conveyer, and then falls into the rotating cylinder. The fire-box is heated to a high temperature, and hot gases driven by a fan connected to it pass through the rotating cylinder, then through the forewarmer, and finally through a dust chamber to the chimney. The strong draught of hot gases causes the fragments of gypsum to travel in the same direction with a velocity inversely proportional to their size, so that the largest pieces are exposed to the heat for a longer period than the finer particles. The heat is so well utilised that the temperature of the gases passing to the chimney is only about 80° C.

The **Cummer rotary calciner** is much used in the United States. The raw material, which is first crushed and screened until it will pass through a 1-in. ring, is fed through a hopper into a cylinder, which is mounted on trunnions, so that it rotates about a slightly inclined axis. As the material passes down the cylinder it is picked up and again dropped by the lifting blades attached to the inner surface of the latter, thus being thoroughly exposed to the action of the hot gases. The latter are drawn by means of a fan into the brick chamber which surrounds the cylinder, and sufficient cold air is introduced through two registers to cool them to the required temperature, after which they are drawn into the cylinder through an opening, and, passing along in the opposite direction to the raw material, escape through the other end to the chimney. Pyrometers are inserted through the holes in order to control the temperature. The calcined material is immediately conveyed by means of an elevator to the calcining bins, where the heat still remaining in the material completes the calcination, and the cool plaster is finally ground, passed through sieves, and placed in sacks.

Calcining in Kettles.—This was the most common method of preparing plaster of Paris in the United States, but although superior to the old-fashioned European processes, it is slow and expensive, and is therefore being gradually abandoned in favour of rotary kilns.

The gypsum is first ground and then charged into cylindrical iron kettles about 8-10 ft. in diameter and 6-8 ft. high, through which pass two or four horizontal flues about 12 in. in diameter. The "kettle bottom" usually consists of a concave-convex iron casting with the convex side placed upwards, but in modern plants sectional kettle bottoms are frequently employed. The sides of the kettle are of boiler plate about $\frac{3}{8}$-$\frac{5}{8}$ in. thick, and the top is covered in by means of a sheet-iron cap provided with a door which serves for the introduction of the raw material. The kettles are supported on and enclosed by masonry, and a fire space, shaped like an inverted cone, is left underneath each kettle. The first floor of the mill is about a foot from the top of the kettles, which are usually arranged in pairs, with a shoot for supplying the raw material, and a pit for the calcined material to each pair. As it is necessary that the contents of the kettles should be kept constantly stirred, each of the latter is provided with paddles driven from an overhead shaft.

On starting a kettle, the heat must be gradually applied whilst the raw material is being fed in, and the contents must be kept constantly stirred. As the temperature rises to about 105°-110° C. the contents appear to boil violently until the mechanically held water is driven off through a stack passing through the sheet-iron cover, after which they settle down. On heating to 143° C., however, the boiling commences again as the combined water begins to be driven off. When the water of hydration has been driven off, the hot, finished material is run into the fire-proof pit until it has slightly cooled, when it is passed through a revolving wire screen in order to separate all large particles and coarse foreign matter, and is finally conveyed to the storage bins.

Grinding.—The grinding may be carried out either before or after the calcination, the latter being the most usual method in Europe, and also being used in America where rotary calciners are employed.

In either case the grinding is a simple matter. When the plaster-stone is ground before calcination the operation is usually carried out in three stages. The stone is first crushed to lumps about 2-4 in. in diameter in a coarse crusher. The roughly crushed material is then passed on to crushers of the coffee-mill type, which reduce it to about $\frac{1}{4}$-$\frac{1}{2}$ in. in diameter, and is finally ground in fine grinding machines, until about 55-65 per cent. will pass through a sieve containing 100 meshes to the linear inch. It is then ready for calcination. When gypsum-earth is used for the raw material the rough crushers are not needed, and the grinding is carried out in two stages. When the grinding is carried out after calcination it is usually done between millstones, but sometimes edge-runners or rollers are employed. The ground plaster should be kept from contact with air, as it readily absorbs moisture and deteriorates; unfortunately, however, but little attention is usually paid to this detail, and the plaster is placed in sacks after grinding. It is sometimes the practice in France to preserve the plaster in heaps by slightly wetting the surface, so that the crust thus formed protects the remainder of the heap. This plan is at once simple and effective.

Pure plaster of Paris consists of the hydrated calcium sulphate, $CaSO_4 \cdot \frac{1}{2}H_2O$, and therefore contains 93.8 per cent. of anhydrous calcium sulphate and 6.2 per cent. of water. The less pure forms, however, and especially the cement plasters, contain various amounts of silica, alumina, ferric oxide, calcium carbonate, magnesium carbonate, and other impurities.

Le Voisier[1] was the first to show that the change from gypsum to plaster of Paris during calcination was due to the loss of water, and that the hardening of the plaster after gauging was due to the absorption of water to reform the original compound. Le Chatelier[2] has proved that plaster of Paris is a definite hydrate, $2CaSO_4,H_2O$, and has shown that when water is added to the calcined plaster a solution is obtained from which the hydrated sulphate soon crystallises out, thus allowing more of the plaster to be dissolved; this alternate solution and crystallisation continues until the whole of the plaster has become hydrated, the two processes going on simultaneously at different parts of the mass. According to Rohland,[3] the hardening of calcined plaster with water is a colloidal process.

The specific gravity of plaster of Paris is about 2.58. The tensile strength is about 300-400 lbs. per square inch for neat plaster, and 100-200 lbs. per square inch for a mixture of one part by weight of plaster to three of sand.

Retarders and Accelerators.—Plasters made from impure gypsum are usually sufficiently slow setting, but pure plaster of Paris sets with extreme rapidity, and, in order to moderate this action, it is a common practice to add various substances known as **retarders** to the cold calcined plaster.

The materials mostly employed for this purpose are glue, sawdust, blood, and other substances of animal or vegetable origin. Sometimes it is required to hasten the setting of an impure plaster, in which case an **accelerator** is employed. These are crystalline salts, one of the most efficient being sodium chloride.

A recent development is the use of urea formaldehyde resin with plaster of Paris for moulding compositions. The plaster is mixed into a paste with the water-soluble resin, and the mixture gradually sets into a waterproof, hard, compound that takes a beautiful polish.

Hardening Plaster.—Plaster of Paris may be hardened by the addition of various substances. A solution of glue or gum arabic may be employed, as in the preparation of "stucco" (see p. 126), or the plaster may be mixed with a little freshly slaked lime, and the casting dipped in a strong solution of magnesium sulphate. Another method is to use a solution of sodium silicate (water-glass), but the most usual plan is to use a solution of alum, as in the preparation of the "hard-finish" plasters (see below, and on p. 126).

The casting may be placed in the alum bath for some weeks, and then slowly dried, or the plaster may be soaked in the solution, dried, and again calcined. Still another method consists in mixing the plaster with a little finely ground mallow root, and kneading the mixture in water, or in gauging the plaster with a decoction of mallow root.

Flooring Plasters.—Flooring plasters (*Estrichgips*) are employed to a very large extent in Germany, as they give a hard and durable surface which is very suitable for floors, etc. They are prepared by coarsely crushing a relatively pure plaster-stone, and calcining it in a vertical kiln at a temperature of about 400°-500° C. for not more than four hours. If the heating be continued for a longer period than this the plaster becomes entirely deprived of its setting properties. The fuel employed is generally coal, and is burnt on a grate at the side of the kiln, the hot gases passing through the mass of the gypsum. The calcined stone is then very finely ground. The flooring plasters set with extreme slowness, but finally acquire great hardness. They consist essentially of anhydrous calcium sulphate, $CaSO_4$.

According to Van't Hoff when gypsum is completely dehydrated its ability to combine with water is at first only retarded, but gradually becomes lost either by prolonged exposure to a high temperature or by submission to more intense heat. Hence the necessity for keeping the temperature at 400°-500° C., and for discontinuing the calcination after four hours.

Hard-Finish Plasters.—These plasters resemble the flooring plasters in consisting essentially of anhydrous calcium sulphate, but they are calcined at a higher temperature (sometimes at a red heat) and are usually treated with various chemicals, such as alum, during the process of manufacture. The calcination is carried out in two stages, the plaster-stone being first calcined, then dipped in a solution of alum, borax, or other salt, and again calcined at a high temperature, after which it is finely ground.

---

[1] Le Voisier, *Œuvres Completes*, 17, 3, 122.

[2] Le Chatelier, *Compt. Rend.*, 1883, 96, 715; *Annales des Mines*, 1887 (8), 11, 345; "Rech. Expt. sur la Constitution des Mortiers Hydrauliques," 1904.

[3] Rohland, *Kolloid Zeitsch.*, 1913, 13, 61.

Keene's cement is now the general name for a number of different plasters prepared by various manufacturers, the original patent having expired. It is usually prepared by first calcining the plaster-stone to plaster of Paris, dipping this in a solution of alum or aluminium sulphate, drying, and recalcining at a much higher temperature. Sometimes, however, the first calcination is carried out at a high temperature, even red heat, and sometimes other salts are used instead of alum; indeed in some cases the plaster is prepared without dipping in any solution, when it is of course really a flooring plaster.

Mack's cement is prepared by adding calcined sodium sulphate or potassium sulphate to completely dehydrated gypsum. It sets rapidly and becomes very hard and durable. **Martin's cement** is similar to Keene's, but the solution of alum is replaced by one of potassium carbonate.

Parian cement may also be prepared in the same manner as Keene's cement, employing, however, a solution of borax in place of alum; or it may be manufactured by burning an intimate mixture of powdered gypsum and dry borax and finely grinding the product. All these plasters set quickly and become hard and durable.

MORTAR, CONCRETE, PLASTER, AND STUCCO

Mortars.—Mortars are divided into **common mortar**, which is made with lime, and **cement mortar**, which is made with Portland, natural, or slag cement. **Common mortar** is prepared by mixing lime with water and sand; the proportions taken vary somewhat with the quality of the lime, but are usually one part by measure of slaked lime to three parts by measure of sharp sand, with enough water to make a somewhat stiff paste.

Small quantities of mortar are mixed by hand, but when large amounts are required it is usual to employ some form of mixing machine. The sand used should be free from clayey matter or vegetable earth, and should consist of sharp angular fragments of silica, though sands derived from granites and containing a large proportion of feldspar are also valuable. Sand which is much water worn, and blown sand, are not suitable, because they consist of more or less rounded fragments, and blown sand is also too finely grained. Sea sand is also unsatisfactory because of the deliquescent salts which accompany it. These salts may, however, be washed out by prolonged exposure to the weather or by washing in running water. Artificial sands, such as crushed sandstone, quartzite, granulated blast furnace slag, etc., are also used for mixing in mortar. The sand is mixed with the lime in order to reduce the shrinkage and prevent the consequent cracking which takes place when a paste of lime and water alone is allowed to dry, to render the mass more porous—thus facilitating the absorption of the carbon dioxide upon which the ultimate hardening of the mortar depends, and to somewhat increase the resistance to crushing. It also lessens the cost of the mortar, because sand is cheaper than lime. Sometimes trass, puzzuolana, or other natural or artificial puzzuolanic material is mixed with the lime (see p. 83).

Cement mortar may consist of a mixture of natural slag or Portland cement, sand and water, but as this does not spread freely it is a common practice to add more or less lime, or sometimes loam, although these materials (especially the latter) are detrimental to the strength of the mortar.

Cement mortar is employed for masonry structures, which are exposed to the action of running water or of waves, as a coating to cover masonry or concrete walls, and for other purposes.

Concrete.—Concrete or **Béton** consists of a conglomerate of pebbles, broken stones, gravel, blast furnace slag, or sometimes cinders, known as the aggregate, embedded in a matrix of mortar, the amount of mortar employed being sufficient to fill all the voids between the stones. The mortar may be either hydraulic lime mortar, as in the case of ancient or mediæval concrete, or cement mortar as in most modern work.

A distinction is sometimes made between the terms concrete and béton, the former term being used when the lime or cement is mixed with the gravel before adding water, as is usually the case in this country, whilst the latter term is employed when the lime is worked into a paste before adding the gravel. Concrete is used for making blocks of artificial stone of various sizes for building purposes and for paving, for the production of monolithic work, and as a backing for coursed masonry. As in the case of mortar, it may be mixed by hand or by machinery, a great variety of machines for this purpose being in use.

Armoured or Reinforced Concrete.—For some years it has been the practice to employ concrete in which iron rods, wire netting, or perforated iron plates are embedded. The material thus obtained is known as *armoured, reinforced* or *ferro concrete* (see also p. 129).

It is used to a large extent in the construction of arches, pillars, beams, floors, etc., and also for making pipes and tiles.

Plasters.—The ceilings and inside walls of buildings are usually given a smooth coating of plaster.

In France, plaster of Paris is employed for this purpose, but in England it is more usual to employ a lime mortar to which cows' or calves' hair is added. The various "hard-finish" plasters (see p. 116), such as Keene's and Parian cements, are also used and, especially for outside work, cement mortar.

Stucco.—Stucco is a special hard plaster which can be polished. It is usually coloured so as to imitate various kinds of marble.

There are two principal kinds of stucco, that made from plaster of Paris, and that made from lime. **Plaster stucco** is mixed with a lukewarm solution of size, fish-glue, or gum arabic. When required of any particular colour, the colouring matter is dissolved in the solution before gauging. **Lime stucco** is generally mixed with chalk, plaster, or other materials; the colours are usually obtained by mixing metallic oxides and salts with the lime. Cement plaster is also known as **cement stucco** when it is employed for coating the surfaces of walls, pillars, etc., white Portland cement being particularly suited for this purpose.

Staff.—For temporary buildings of an ornamental character, such as those required for exhibitions, etc., it is usual to employ a plaster which is toughened and bound together by means of tow, or sometimes by asbestos or slag wool. This material, which is known as **staff** or **fibrous plaster**, is fixed upon a backing of very coarse, open canvas called "scrim."

WATERPROOFING CEMENT MORTAR AND CONCRETE

It is often necessary that cement concrete should be impermeable to water, as in the construction of reservoirs, sewers, and so forth. In such cases it is usually quite possible to make the concrete watertight by using a properly graded aggregate, and completely filling the voids with mortar made with cement and fine sand, but it is a common practice to have recourse to some method of rendering the cement waterproof.

Sometimes cement work already in existence also often has to be rendered watertight, and in this case it is necessary to add a coating of some waterproofing material. This may be done by covering the surface with some impermeable material, such as asphalt, tar or paint, or by applying alternate coatings of soap and alum solution by means of a brush, as in **Sylvester's process**, the object being to fill the pores of the concrete or mortar with an insoluble precipitate. In the case of new work the materials—soft soap, alum, potash, etc., are sometimes mixed in with the mortar, and since **Moyer**[1] has shown that when mineral oil is mixed with cement mortar a waterproof mixture is obtained, this method of waterproofing is sometimes employed. Animal or vegetable oils should not be used in place of the mineral oil because they are liable to decompose, with the liberation of free fatty acids.

A large number of compounds of very varying efficiency have been introduced for this purpose under more or less fancy names,[2] such as "**ceresit**," "**driwal**," "**impervite**," and "**cement kote**." So far as the author is aware all the compounds hitherto introduced fail when exposed to water under a high pressure, and many have a more or less harmful effect upon the cement, a reduction of as much as 30 per cent. in strength being sometimes found. A large number of these compounds consist essentially of calcium carbonate, alum and calcium soap, sometimes with more or less free oil or fat. They are usually sold either in the form of a powder to be mixed with the dry cement before adding the water, or in the form of a paste to be mixed with the water used for gauging. One of the best compounds of this water-repellant type which has come under the author's notice is known as "**medusa**." When mixed with proper care this compound, which is a fine, white, extremely water-repellant powder, proves satisfactory for the purpose for which it is intended. Another class of water repellants which has been recently introduced consists of **mineral oils.**

---

[1] A. Moyer, *Concrete and Constructional Engineering*, 1910, **5**, 166.
[2] W. L. Gadd, *ibid.*, 1908, **3**, 154; *Journal of the Concrete Inst.*, 1912, **4**, 503.

Some waterproofing compounds consist of solutions of sodium silicate (waterglass) or silicofluoride, and other silicofluorides such as those of zinc, magnesium, and aluminium are also used, being sold under the name of **fluates.**

One compound consists essentially of a mixture of alum and zinc sulphate in a quantity of water which is insufficient for complete solution, and another consists of a solution of oxalic acid. The object in all these cases is to form insoluble compounds of calcium in the pores of the mortar or concrete.

Other compounds depend upon the presence of, or are stated to contain asphalt, or some other bituminous substance for their waterproofing properties.

Surface Hardening

The surface treatment of concrete with sodium silicate solutions is an effective method of hardening the surface, preventing dust formation, and reducing alkalinity and water penetration. The most suitable silicate to use is that containing the highest ratio of silica to sodium oxide, the type sold as P. 84 by I.C.I. Limited being very suitable. The excess of silica in the solution combines with calcium hydroxide to form hard, insoluble calcium silicate, which binds together the surface layers and reduces porosity. The maximum effect is obtained when a small proportion of sodium silicate, for example 2 per cent. of the weight of cement, is added to the gauging water before mixing. This causes a serious reduction of strength in the finished concrete, so the method is only recommended for acid resisting mortars, such as the pointing between sewage blocks.

Acceleration of Set by the Use of Calcium Chloride

Calcium chloride has a marked effect upon the setting of cement, the addition of as little as 0.5 per cent. to the gauging water causing the accelerated development of strength in ordinary cement, so that it can be used in place of rapid hardening cement. The calcium chloride forms insoluble stable complexes with the cement matrix, and reduces the proportion of calcium hydroxide liberated during the setting processes.

CHEMICAL ANALYSIS OF LIMES AND CEMENTS

Gravimetric methods for the analysis of inorganic compounds, such as limes and cements, have changed but little during the last fifty years. For rapid volumetric or colorimetric methods of analysis, see a modern book on inorganic analysis, such as "Standard Methods of Chemical Analysis" by W. Scott and N. H. Furman, New York and London, 1946.

The following methods may be used for a preliminary examination of calcareous cements.

Common and Hydraulic Limes.—The **water** and **carbon dioxide** in these limes are determined by igniting a weighed amount in a platinum crucible and ascertaining the loss of weight. The carbon dioxide is then determined by any of the usual methods, that of Schrötter being very suitable; the difference between this value and the loss on ignition gives the amount of water present. In order to determine the **lime** and **magnesia,** which is frequently all that is necessary, a weighed amount of the sample is dissolved in hydrochloric acid, the solution rendered alkaline with ammonia, boiled, and the precipitate of silica, alumina, and ferric oxide filtered off, dried,

---

[1] J. W. Mellor and H. V. Thompson, "A Treatise on Quantitative Inorganic Analysis." London, 1938.

ignited, and weighed. The lime is then precipitated from the filtrate in the form of calcium oxalate, filtered off, dried, ignited to the oxide, cooled, and weighed. The magnesia in the filtrate from the calcium oxalate is determined as magnesium pyrophosphate, $Mg_2P_2O_7$, in the usual manner.

The calcium oxide in common lime may be determined by boiling about 0.5 g. of the sample in about 250 c.c. of air-free distilled water, cooling and titrating the cold solution with $\frac{N}{10}$ HCl, using phenolphthalein solution as an indicator.

$$\frac{\text{No. of c.c. } \frac{N}{10} \text{ HCl used} \times 0.0028 \times 100}{\text{Weight of sample}} = \text{percentage of calcium oxide.}$$

Portland Cement.—A weighed amount of the dried cement is placed in an evaporating dish and triturated with a little water until all tendency to set has ceased. Hydrochloric acid is then added and the contents of the dish evaporated to dryness, then baked at a temperature of 200° C. for about an hour and allowed to cool. More acid is added, and the process repeated, after which the dry mass is treated with dilute hydrochloric acid, boiled, filtered, and washed, the filtrate and washings being made up to 250 c.c. at 15° C. The residue consists of **silica** and **insoluble** matter, which are separated in the usual manner by fusion with sodium carbonate. A known volume of the 250 c.c. of solution is now transferred to a beaker, rendered alkaline with ammonia, warmed, filtered, and the precipitate, which consists of **ferric oxide** and **alumina**, washed, dried, and ignited. These oxides may be separated and determined gravimetrically, but owing to the difficulty of carrying out a complete separation, it is better to dissolve up the weighed precipitate and then estimate the iron volumetrically by means of potassium permanganate or dichromate, and take the difference as the amount of alumina.

If it is required to determine the **ferrous iron**, this is done by triturating a few grammes of the cement with an excess of water until all tendency to set has ceased, adding a little sodium bicarbonate, and washing the mixture into a flask fitted up in the usual manner for solution in absence of air, dissolving the cement in hydrochloric acid, and determining the iron by titration with potassium bichromate.

The **lime** and **magnesia** in the filtrate and washings from the combined precipitate of ferric oxide and alumina are determined in the same manner as in the analysis of lime (see above).

The **sulphur** in the form of **sulphuric anhydride** is determined by adding a solution of barium chloride to a known volume of the 250 c.c. of solution (see above), and collecting the precipitated barium sulphate, which is dried, ignited, and weighed. The sulphur present, in the form of **sulphides,** may be determined by dissolving a known amount of the sample in hydrochloric acid in the absence of air, passing the evolved gases through a solution of cadmium chloride, and weighing the precipitated cadmium sulphide.

The **alkalis** may be determined by **Laurence Smith's** method,[1] and the **carbon dioxide and water** may be determined in the same manner as in the analysis of lime.

Scott and **Furman**[2] (*loc. cit.*) give a number of methods for the estimation of the constituents of cements, many of which have been used as tentative standards by the U.S. Bureau of Standards and the A.S.T.M. Amongst the methods not included above are the following:—

Silica is determined by rendering insoluble by evaporating to dryness with hydrochloric acid. The result is checked by treatment with hydrofluoric acid.

Magnesia is determined volumetrically by the titration of magnesium oxyquinolate.

Phosphorus may be determined colorimetrically by the molybdate method.

Manganese is determined by titration with sodium arsenite solution in the presence of nitric acid.

B.S. Method of determining insoluble residue (B.S. 12, 1947)

The cement is boiled for 10 minutes with a dilute solution of HCl, filtered and washed ten times with hot, distilled water. The residue is then boiled for 10 minutes with twice normal Na_2CO_3 solution, again filtered and washed five times with water, then with dilute HCl, and then with water till free from chlorides. The filter paper and contents are then dried, ignited, and weighed as "insoluble residue."

---

[1] W. Scott and N. H. Furman (*loc. cit.*).

[2] A.S.T.M., Tentative Methods for Analysis, C. 114-37 T, 1937.

Natural Cements, High Alumina Cements, Slag Cements, and Plaster of Paris

These are analysed in the same manner as Portland cement.

PHYSICAL AND MECHANICAL TESTS

Portland cement, being the most important of the calcareous cements, is the one most frequently submitted to physical and mechanical tests, and when other cements are tested they are treated in much the same manner. The chief physical and mechanical tests are:—

- Fineness.
- Tensile strength.
- Constancy of volume and soundness.
- Crushing strength.
- Setting time.

Before carrying out the tests for tensile and crushing strength, setting time, and soundness, the cement should be spread out for a depth of 3 ins., and kept at a temperature of 15°–18° C. for twenty-four hours.

Specific Gravity

Specific gravity is no longer considered to be a guide to the quality of a cement, and this determination is now omitted from British and Continental Standard Specifications. The physical tests listed above are included in the latest British Standard Specification for Portland cement, ordinary and rapid hardening grades (B.S. 12, 1947).

Fineness.—The degree of fineness of the cement is of the utmost importance, and during recent years far more attention has been paid to this point than was formerly the case. The fineness is tested by means of sieves of brass wire cloth, which must be woven and not twilled.

The sieve must comply with the requirements of Table I. of B.S. 410, "Test Sieves." The standard test for fineness is to sieve continuously for 15 minutes, 100 gm. of cement on a B.S. test sieve, No. 170. The residue by weight must not exceed the following values:—

For ordinary Portland cement - - -	10 per cent.
For rapid hardening Portland cement - -	5 ,,

An alternative is to measure the specific surface of the cement caused by an air permeability method. For details of the method, which necessitates the measurement of density, see B.S. 12. The specific surface of cements should not be less than:

2,250 sq. cm./gm. for ordinary Portland cement, or
3,250 ,, ,, ,, rapid hardening Portland cement.

Tensile Strength.—Tests for tensile strength were among the first to be carried out in the mechanical testing of Portland cement, and they are still almost universally employed in this country, although a knowledge of the tensile strength is comparatively useless because, in the great majority of cases, it is only the compressive strength that matters.

A mixture of one part by weight of cement and three parts by weight of a standard grade of sand from Leighton Buzzard are gauged with water according to the formula:

$$\frac{0.78P}{4} + 2.50$$

where P is the percentage of water required to produce a paste of standard consistency, according to B.S. 12, Appendix C.

It is then moulded in brass or gun-metal moulds, which should be wiped with an oily cloth before filling. The shape of the briquettes employed at different times has varied considerably, but that shown in Fig. 34 is the usual modern form, and the one recommended by the British

Standard Specification (1947). The briquettes are kept in a damp atmosphere for twenty-four hours after gauging, and are then placed in clean water at a temperature of 15°–18° C. (59°–64° F.) until

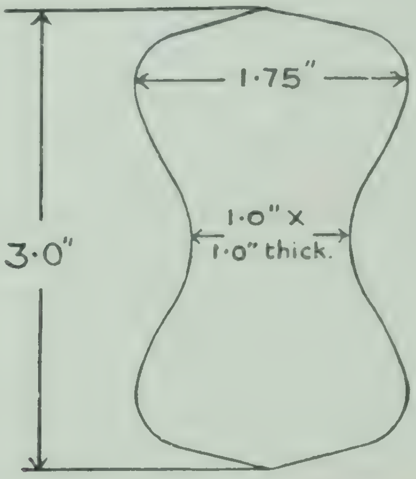


Fig. 34.—Test Piece.

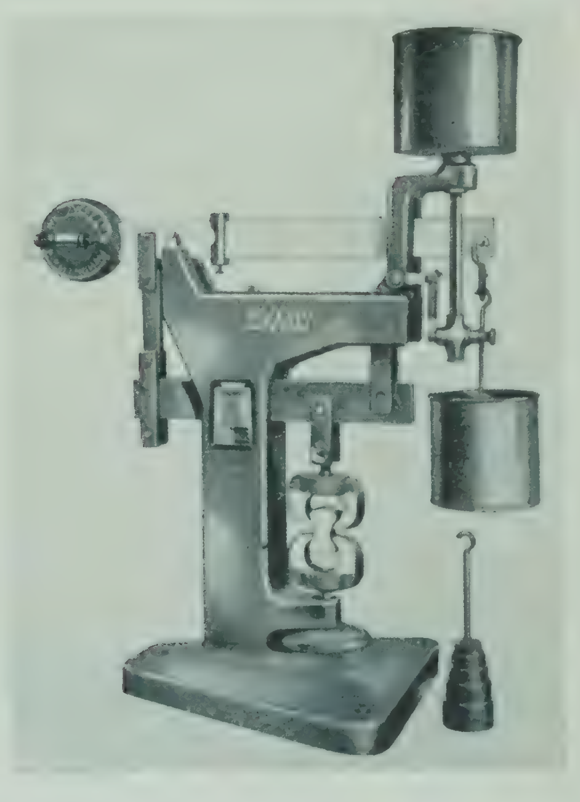


Fig. 35.—Avery Cement Testing Machine.

required for breaking; if they are to be kept for more than a week the water must be changed every seven days. They are tested for tensile strength immediately after being removed from the water. The machines for breaking the briquette vary very considerably in design, one of the best being the **Avery Testing Machine**, shown in Fig. 35. According to the British Standard

Specification (1947) the briquettes are to be prepared without ramming or hammering in any form, and are to be tested at seven and twenty-eight days.

The average tensile strength of six briquettes, prepared and stored in the above manner, should be as follows:—

Ordinary Portland Cement

After 3 days—not less than 300 lbs./sq. in.
After 7 days—greater than after 3 days and not less than 375 lbs./sq. in.

Rapid Hardening Portland Cement

After 1 day—not less than 300 lbs./sq. in.
After 3 days—greater than after 1 day and not less than 450 lbs./sq. in.

Crushing Strength.—The compression test is of much greater importance than the tensile test, although it is not so frequently employed, at any rate in this country.

According to B.S. 12, 1947, cubes of dimensions 2.78 ins. are made of a mixture of the following composition:—

Cement	185 gm.
Standard sand	555 „
Water	74 „

Each batch is mixed separately and placed into a collapsible metal mould, which is then vibrated for two minutes in a standard vibration machine. After vibration the cubes are kept at 61° F. ±1° (16.1° C. ±0.55°) in an atmosphere of at least 90 per cent. relative humidity for 24 hours. They are then stored in water, as for the tensile test, till required. In the test, three cubes are examined for each period of storage. The compression machine used, which may be of any standard design, is much more robust than the tensile strength machine, and the load should be increased at a constant rate of 5,000 lbs./sq. in./min. A modern form of machine made by W. & T. Avery Ltd. is shown in Fig. 36. The following compressive strengths are required:—

Ordinary Portland Cement

After 3 days—not less than 1,600 lbs./sq. in.
After 7 days—greater than after 3 days and not less than 2,500 lbs./sq. in.

Rapid Hardening Portland Cement

After 1 day—not less than 1,600 lbs./sq. in.
After 3 days—greater than after 1 day and not less than 3,500 lbs./sq. in.

Setting Time.—The setting time of cement is not usually of great importance, except in the case of quick-setting cements, when it is an indication of the length of time during which the cement may be worked during gauging. It is divided into two periods, known respectively as the **initial set**, and the **final set** or **set hard.** The time of the initial set is the period between the addition of the water and the moment when the mass loses its fluid condition, and the final set is the period between the addition of the water and the moment when the cement is sufficiently hard to withstand a specified pressure. The initial set is sharply defined in quick-setting cements, but is very vague and ill-defined in those which are slow setting. As the setting time is affected by the amount of water used and the temperature of the room in which the test is carried out, the paste must be made of a specified consistency, and the test should be carried out at a definite temperature, usually at 15°–18° C. Both the initial and final setting time are determined by means of the **Vicat needle**, shown in Fig. 37. The needle is 1 mm. square, and is loaded to 300 g. The cement is contained in a split ring 8 cm. in diameter and 4 cm. high, which rests on a glass plate.

For the determination of initial set, according to B.S. 12, 1947, the needle is gently lowered into contact with the surface of the test block, quickly released and allowed to sink into the same. This process is repeated until the needle, when

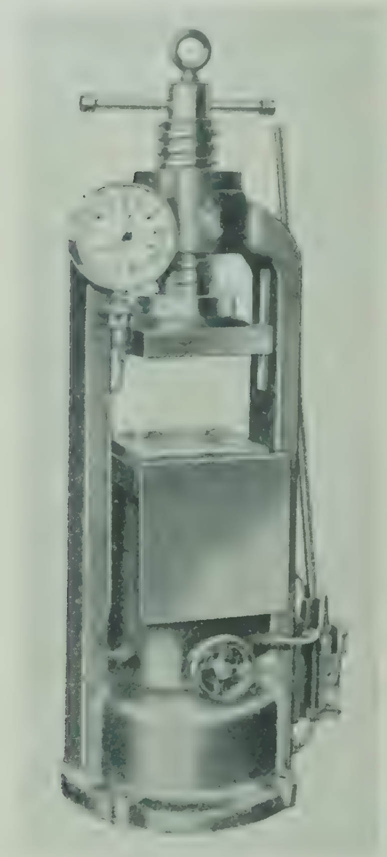


FIG. 36.—Avery Compression Testing Machine.

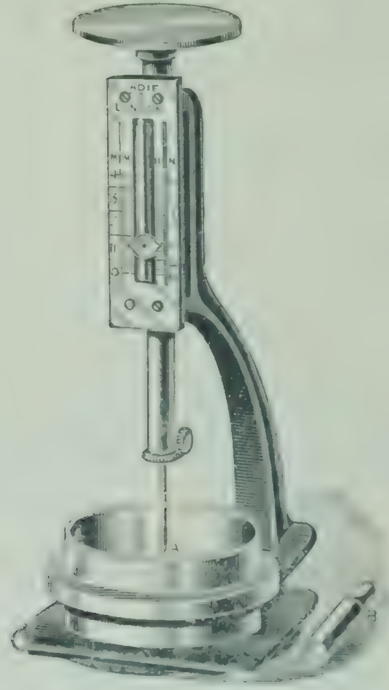


FIG. 37.—The Vicat Needle.

brought into contact with the test block and released as above, does not pierce it by about 5 mm. from the bottom of the mould. The period elapsing between the time when the water is added to the cement and the time at which the needle ceases to pierce the test block completely is taken as the initial setting time.

For the determination of the final setting time the needle of the Vicat apparatus is replaced by a needle with an annulara ttachment shown in Fig. 37 of B.S. 12, 1947. The cement is considered as finally set when, upon applying the needle gently to the surface of the test block, the needle makes an impression thereon, while the attachment fails to do so. In the event of a scum forming on the surface of the test block, the underside of the test block may be used for determining the final set.

The setting times of the cement, when tested as above, should be:—

Initial setting time—not less than 30 minutes.
Final setting time—not less than 10 hours.

Constancy of Volume and Soundness.—The tests for constancy of volume and soundness are the most important of the mechanical tests. Soundness was formerly attributed to the presence of free lime, due to over-liming or under-burning, which slaked and expanded after the setting of the cement, causing the latter to "blow." At the present time this view is somewhat modified by most cement chemists. Ordinary quicklime undergoes immediate hydration on the addition of water, and therefore, even if present, could not be the cause of any subsequent expansion; but when the lime exists in a more or less crystalline form the hydration takes place much more slowly. The expansion of cement after setting may therefore be due to the presence of lime in a more or less crystalline form, in excess of that which the alite is capable of holding in combination or in solid solution, or it may be due to the presence of an excess of magnesia, or to an excessive proportion of sulphates. The expansion in the latter case is considered by **Candlot** to be due to the formation of calcium sulpho-aluminate. Many methods have been proposed for carrying out the test for change of volume and soundness; at the present time an accelerated test is generally employed. In the **Faija test** a freshly gauged pat, placed on a glass plate, is subjected to a temperature of 40.5°–43° C. in a moist atmosphere until set, and is then immersed in water at a temperature of 46°–49° C. for the remainder of twenty-four hours. If the pat does not show any cracks or blisters on the surface next the glass the cement is considered to be sound, otherwise the sample is spread out in a thin layer in a cool dry place for a day or two and the test repeated. If this second pat does not show any cracks or blisters the cement is considered sound when properly aerated. The **Le Chatelier test** is usually employed. The apparatus consists of a split brass ring, 30 mm. in diameter and 30 mm. deep, to which two pointers, 150 mm. in length, are soldered (one on each side of the split). The ring is placed on a glass plate, filled with the cement paste, covered over with a second glass plate, and the whole placed in water at 15°–18° C. for twenty-four hours to set. The distance between the ends of the pointers is then measured and the apparatus is placed in cold water, which is then gradually raised to the boiling point, and kept boiling for six hours. After cooling, the distance between the ends of the pointers is again measured, the increase in the distance being termed the **expansion**. According to the British Standard Specification (1947) the soundness of Portland cement must be determined by the Le Chatelier method, and the expansion must not exceed 10 mm. when the sample has been aerated for twenty-four hours in the manner described on p. 124. If the expansion is greater than this limit the test must be repeated, with the difference that the sample is aerated at 15°–18° C. for seven days before testing. In this case the expansion must not exceed 5 mm.

SPECIFICATION FOR HIGH ALUMINA CEMENTS

(*cf.* B.S. 915, 1940)

Setting Time

For the determination of setting times, ciment fondu is gauged neat with 22 per cent. by weight of water and the test using the Vicat needles carried out as with Portland cement. The setting times are from 2–4 hours for the initial set and 30 minutes later for the final set.

Fineness

This is normally such that about 6 per cent. remains on a 170-mesh B.S. sieve.

Soundness

The expansion of ciment fondu, as measured by the standard Le Chatelier calliper, is zero.

Strength

When testing for strength, a 3 : 1 sand mortar mix, 10 per cent. by weight of water is used on the dry materials. When testing 1 : 2 : 4 concrete the amount of water should be 60 per cent.

The compressive strength of cement is determined on 3 : 1 standard mortar cubes in accordance with B.S. 915, 1940. The compressive strength after 24 hours should not be less than 6,000 lbs. sq. in., and after 3 days not less than 7,000 lbs. sq. in. The strength of good quality ciment fondu cubes is usually much greater than these minimum requirements.

Resistance to Shear

The resistance to shear of 1 : 2 : 4 ciment fondu concrete is approximately as follows:—

1 day	1,750	lbs./sq. in.
3 days	2,060	,,
7 days	2,300	,,
28 days	2,500	,,

Specific Gravity = approximately 3.1.

The weight per cu. ft. varies with the method of manufacture, and varies from about 80-110 lbs. An average of 90 lbs. per cu. ft. may be taken as a good average figure, as with Portland cement.

High alumina cement has setting times comparable with those of Portland cements, but it gains strength rapidly. The relative rates of increase in strength of high alumina cement, rapid hardening Portland cement, and normal Portland cement are shown in Fig. 38, from the paper by Lea (*loc. cit.*).

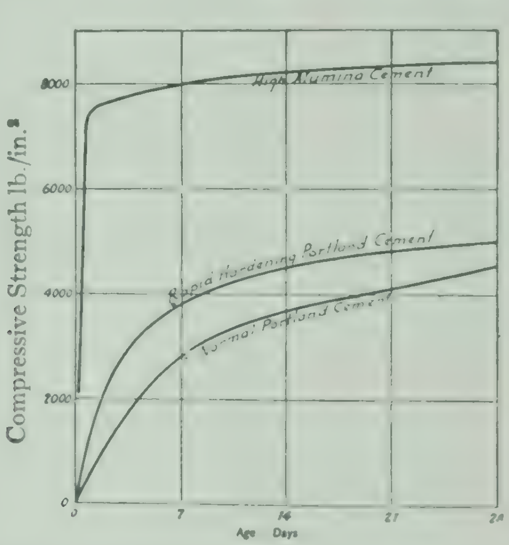


FIG. 38.—Relation Strengths of Cements. 1 : 2 : 4 Concrete Mixes.

Refractory Concrete

Ciment fondu, or high alumina cement, has excellent refractory properties and, when mixed into concrete, using suitably crushed aggregate as a grog, the product may be used for high temperature furnaces, either as a patching cement, as a moulded product, or in precast brick or slab form. The following table, from the publication "Refractory Concrete" by the Lafarge Aluminous Cement

Co., shows the melting points of the constituents of aluminous cements and their eutectics:—

Calcium Aluminates.		Eutectics.	
$3CaO, 5Al_2O_3$	1,720° C.	C_3A/C_5A_3	1,395° C.
CaO, Al_2O_3	1,600° C.	C_5A_3/AC	1,400° C.
$5CaO, 3Al_2O_3$*	1,455° C.	C_3A_5/AC	1,590° C.
$3CaO, Al_2O_3$	1,535° C.	C_3A_5/A	1,700° C.
Other constituents:	$SiO_2, Al_2O_3, 2CaO$		1,590° C.
	$Al_2O_3, Fe_2O_3, 4CaO$		1,415° C.
Aluminous cements			1,400° C.

* Now regarded as $12CaO, 7Al_2O_3$.

In the manufacture of these products it is important to grade the crushed refractory brick used as grog into two sizes, such as material through $\frac{3}{8}$ in. on $\frac{1}{8}$ in. sieve, and through a $\frac{1}{8}$ in. mesh sieve. A typical mix will then be:

Coarse aggregate ($\frac{3}{8}$–$\frac{1}{8}$ in.)	$2\frac{1}{2}$ cu. ft.
Fine aggregate ($\frac{1}{8}$ in.)	$2\frac{1}{2}$ cu. ft.
Ciment fondu 1 cwt.	= 1 cu. ft.

Such a mix, using fire-brick as aggregate, will show a heating curve under load similar to that shown in Fig. 39, taken from the publication "Refractory Concrete."

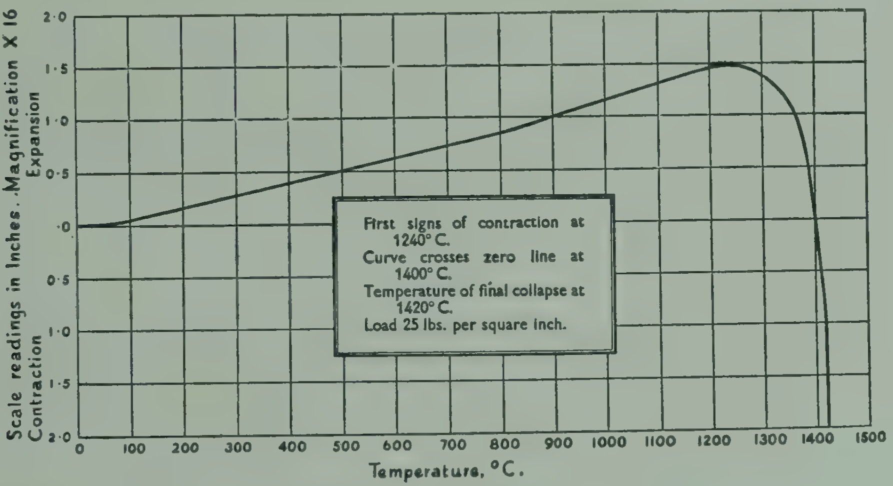


FIG. 39.—Refractoriness under Load Test—Normal Method.
Grog Mixture, 20 per cent. Ciment Fondu—Rate of Heating, 10° C. per min.

For further details of the use of ciment fondu as a refractory see this publication, which may be obtained from the Lafarge Aluminous Cement Co. of London.

Cement and Sulphuric Acid

For details of processes for making cement and sulphuric acid from calcium sulphate, see Martin, Vol. I., Section XIX.

MICROSCOPIC EXAMINATION

A microscopic examination of cement is often of value for detecting the presence of adulterants. Thus, Kentish rag can be distinguished from clinker by its light colour and smooth appearance when examined under the microscope. The microscope has played an even more important part however, in the investigation of the constituents of cement clinker and hardened cement. The earliest attempts to utilise the microscope in this manner were due to **Le Chatelier** and **Tornebohm**, the names "*alite*," "*belite*," etc., by which the constituents of cement clinker are known, being due to the latter investigator. The microscope examination of the clinker may be carried out in two ways: (1) One side of a thin chip of clinker may be ground and polished, the smooth surface cemented to a piece of glass by means of Canada balsam, and the other side then ground until the section is sufficiently thin and polished. The thin section is then removed from the glass, mounted on a microscopic slide, covered with a cover glass, and examined under the microscope by transmitted light. (2) A chip of the clinker is ground and polished on one face only, and examined under the microscope by reflected light, in the same manner as metals and alloys are examined by metallographists. Owing to the difficulty of obtaining sections of sufficient thinness, the second method is to be preferred. The objective should be corrected for use without a cover glass, the most convenient power being a 6 mm., and the eyepiece should be of moderate power so as to give a magnification of about 300 diameters.

In order to polish the clinker it is rubbed on a series of carborundum blocks, or sheets of carborundum cloth or paper, each successive block or cloth being of finer grain than the last; the final polish is then obtained by means of rouge or alumina (diamantine powder) on a piece of stretched cloth. Water must not be used, as it attacks the clinker. When examined under a lens the finished surface should be free from scratches, and should present a mirror-like polish. In order to bring out the structure it is necessary to etch the polished surface by rubbing it on a stretched cloth moistened with water, or by means of a 1 per cent. alcoholic solution of hydrochloric acid.

The following constituents are found in cement clinker:—

Alite.—This constituent is in the form of nearly colourless, well-defined crystals, belonging to the rhombic system. It appears to be the principal product of the chemical reaction between the materials in the kiln, and the quantity found in the clinker increases with the proportion of lime present. According to **Richardson**, alite is a solid solution of tricalcium silicate in tricalcium aluminate (see p. 110). Crystals of pure alite have been prepared, and these were found to contain lime, silica, alumina, ferrous oxide, and magnesia.

Belite.—This is similar to alite, but has a darker colour, and usually shows fine strip. It appears to contain less lime than alite. It is by no means always present in all cement clinker, but is usually found in cements which are poor in lime.

Celite.—Celite and alite are the principal constituents of cement clinker, and are probably the only ones which are essential. Celite is darker in colour than alite, probably on account of the larger proportion of iron which it contains. In the clinker it forms a matrix between the grains of alite, so that it appears to be the more fusible portion of the clinker, which has actually melted at the clinkering temperature and then solidified as a eutectic mixture. An increased amount of ferric oxide in the clinker causes an increased proportion of celite. According to **Richardson**, celite is a solid solution of dicalcium silicate in dicalcium aluminate (see p. 110).

Felite.—This constituent does not often occur in cement clinker, but is found in blast furnace slag. It forms rhombic crystals, and may contain magnesia when this is present in the clinker. Belite and felite are probably two forms of the same solution. According to **Kappen** the proportion of belite to felite in cement clinker depends upon the temperature of the kiln, the production of felite being favoured by a high temperature.

When clinker is etched with 1 per cent. alcoholic hydrochloric acid, and examined by reflected light, it presents the appearance of a number of grains embedded in an intercrystalline matrix. The grains, which are attacked by the etching reagent, consist of *alite*, whilst the intercrystalline portion appears to be mainly *celite*, but often contains more or less of a hard, white, porcelain-like material. A number of gas cavities are always seen, showing that the clinker has an open, pumice-like structure. Clinker from rotary kilns generally presents a much finer structure than that from stationary kilns, otherwise it is essentially the same.

Hardened cement may be polished, etched, and examined in the same manner as clinker. Two constituents are found, the first of which exists in small, irregular grains, embedded in a matrix of the second constituent. The grains consist of unaltered cement clinker, as may be proved by etching with 1 per cent. alcoholic hydrochloric acid, when their structure may be seen. The matrix may be dyed by immersion in an aniline dye, thus showing its colloidal nature (see p. 111). The fact that hardened cement contains unchanged clinker explains why it will again set if re-ground and gauged with water, and also why extremely fine grinding improves cement.

SECTION LX

SOREL CEMENT

By James Shelton, F.I.C.

Revised by Wilfrid Francis

LITERATURE

B.S. 776.—"Materials for Use in the Manufacture of Magnesium Oxychloride Flooring Compositions."
A. W. Comber.—*Chem. and Ind.*, 46, 661 (1927).

It has been found that a paste made by mixing lightly calcined magnesia with a concentrated solution of magnesium chloride sets to a hard mass owing to the formation of a hydrated basic chloride, the composition of which may be expressed by the formula $MgCl_2.5MgO.xH_2O$, the value of x being about 17. This compound is one of the strongest binding materials known, and the mixture of chloride and oxide is technically employed under the name of **Sorel**- (or **Magnesia**-) **Cement**.

The magnesia is obtained[1] by calcining **magnesite**, $MgCO_3$, at a temperature of about 800° C.

The magnesite was formerly burnt in contact with the fuel in shaft kilns, but the modern practice is to employ regenerative gas-fired furnaces. The calcined magnesia should be free from carbonate, as during the setting of the cement the carbonate is decomposed with evolution of carbon dioxide and the production of an unsound cement. The standard quality stipulated for by Continental consumers for Sorel cement contains 85–90 per cent. of magnesium oxide and less than 4 per cent. of lime.

In Germany, **magnesium chloride** is obtained as a by-product from the mother liquor obtained in the extraction of potassium chloride from the deposits of **carnallite**, $MgCl_2.KCl.6H_2O$, at Stassfurt.[2]

The mother liquor, on evaporation at boiling point to a specific gravity of 1.34, deposits magnesium sulphate with chlorides of sodium and potassium. The hot liquor is separated from the crystals and is run into casks in which it solidifies on cooling, and in this state is put on the market as magnesium chloride. *Bittern*, the mother liquor after extraction of common salt from sea water, is another source of magnesium chloride.

For the preparation of sorel cement a solution of magnesium chloride, $MgCl_2$, of specific gravity 1.16-1.26, is employed. Sulphate should have been removed previously by precipitation with barium carbonate. The magnesia is intimately mixed with the aggregate, and the mixture is then moistened with magnesium chloride solution and filled into moulds.

---

[1] See, however, this work, Vol. I., p. 366.
[2] See this work, Vol. I., p. 329, **Stassfurt Industry**, also **Weldon and Deakin Process.**

Mixtures of chloride and oxide of magnesia are sometimes made and sold under the name of dry sorel cement. These are prepared either by simple mixture of chloride crystals with magnesia or by heating the crystals of $MgCl_2,6H_2O$. At temperatures above 180° C. water and hydrochloric acid are evolved from this chloride, and, by judicious heating, a mixture of oxide and chloride in the correct proportions may be obtained (see Patent, No. 8,307, of 1908). The dry sorel cements deteriorate on exposure to the atmosphere and should therefore be packed in soldered tinned iron vessels.

Magnesium oxychloride is one of the strongest cements known. A mixture of 1 part of this cement with 4 parts of sea sand gives a crushing strength of over 8,000 lbs. per square inch. One part of the oxychloride will serve to cement 8 parts of sand. The cement is not appreciably affected by exposure to frost, rain, or occasional flooding, and therefore finds extensive application in the manufacture of artificial stones for building purposes, especially window sills and door-steps, but it is not suitable for stones constantly exposed to water. Owing to its great mechanical strength, this cement is used in the manufacture of abrasive wheels which can be run at a considerable velocity, but such wheels are by no means reliable unless they can be kept quite dry. If employed for wet grinding they soon crack and become dangerous. Silicate cement is not open to this objection (see **Grinding and Polishing Materials**, p. 434). Sorel cement is sometimes employed in the manufacture of **artificial marble** as it is capable of taking a very fine polish.

Many patent flooring compositions contain magnesia cement, and a material known as "xyolite" is composed of sawdust united with this cement. In Hamburg, a flooring which is much in vogue is made by adding magnesium oxychloride to cement sawdust which has been impregnated with oil.

Other fillers for flooring compositions are cork dust, wood flour, asbestos, and inorganic colours. The asbestos commonly used is amphibole asbestos, short fibred or micro-anthophyllite, Cape or Bolivian blue, particularly where mottled coloured effects are required. Flooring of this character is usually waxed so as to obtain a water-resistant surface and to preserve the polish. For domestic and office use and for ships' cabins, Sorel cement flooring is highly prized, for it yields a non-slippy, fireproof surface that is warm to the foot. For factory work it is not so useful, since steam and condensed water attack the surface and cause weak places to develop. It is also corrosive to steel, though this effect can be reduced by replacing part of the magnesium chloride solution by ferrous chloride.

Specifications for materials suitable for the manufacture of Sorel cement compositions are given in the publications mentioned under "Literature."

Other Uses for Sorel Cement.—Sorel cement is an excellent moulding material for structural work, such as window sills, for ornamental work, and for making patterns for engineering or foundry work. When available at a sufficiently low price, as in India and Germany, Sorel cement can also be used in small proportions as a binder for waste powdered fuels in the manufacture of briquettes. (See Vol. I., Section III).

Zinc Oxychloride Cement.—Zinc oxide and zinc chloride form a plastic composition with very similar properties to those of Sorel cement. The two cements may be mixed together in any desired proportions, or used as substitutes for each other. A recent product of this type recently put on the market in Great Britain is called "Pattincrete," or plastic stone. This product has been developed specifically for making permanent patterns and pattern plates for foundry and similar work.

SECTION LXI

ARTIFICIAL STONE

BY JAMES SHELTON, F.I.C.

LITERATURE

W. S. GREY and H. L. CHILDE.—"Concrete, Surface Finishes, Renderings, and Terrazo." London, 1943.

CEMENT MARKETING BOARD.—"Everyday Uses of Portland Cement." London, 1932.

ARTIFICIAL stones are produced by cementing together rock fragments such as quarry waste, sand, mining tailings, etc. Because of their relative cheapness and freedom from flaws, these artificial stones compare favourably with the natural product. The size and shape of the blocks can be varied at will, and ornamental stones are now manufactured which equal in appearance the carved natural stone.

There are several kinds of artificial stone, and as they do not readily admit of classification, they may be described briefly as follows:—

Concrete.—Under the name of concrete, building stones and paving blocks, steps and window sills are manufactured from a mixture of one part Portland cement with three to nine parts of mineral fragments (or **aggregate**), varying in size from fine sand to large pebbles. Steel rods are often embedded in the material in such a position as to take the tensile stresses, the concrete itself being capable of bearing considerable compression (see **Concrete**, p. 125).

Victoria stone is a concrete made of finely crushed granite with a third of its weight of Portland cement. It is usually made from Leicestershire granite which has been washed free from soluble salts, dried, mixed with cement, and the mixture wetted and compressed into moulds. The blocks, when set, are hardened by immersion in a bath of sodium silicate for about a fortnight. Exposure to air effects a further hardening of the blocks, but the hardening is seldom, if ever, complete.

This stone has a crushing strength of over 8,000 lbs. per square inch, and shows a porosity of 1.3 per cent. when immersed for twenty-four hours in water. Iron oxide is often added to impart a red colour to the stone. "Imperial Stone," "Empire Stone," and "Indurated Stone" are concretes of a similar nature.

Ward's stone is a concrete composed of oolitic limestone and Portland cement, and is utilised for ornamental stairways. Another variety of stone sold under this name is composed of granite and Portland cement. **Stuart's granolithic stone** and **Globe granite** are of similar composition.

A concrete made of crushed York stone chippings and Portland cement, hydraulically pressed into moulds, is sold as a paving material under the name of **non-slip stone.**

Clinker and Slagblocks.—In certain districts mixtures of lime with natural puzzuolanic materials, destructor refuse, or granulated blast furnace slag, are utilised for the preparation of building and paving blocks, but they are only used to a limited extent, generally by municipal authorities, or large firms who can find a definite use for them.

Ford's silicate of lime stone is produced by pressing a mixture of burnt lime and sand into a perforated mould. The lime is slaked with boiling water and the stone hardened by exposure to superheated steam for a few hours at a pressure of 120 lbs. per square inch.

Ransome's artificial stone, one of the earliest of this class of material, is prepared by mixing sodium silicate with sand, moulding the mixture to shape, and then immersing in a solution of calcium chloride. A strong bond of calcium silicate is thus formed and the sodium chloride is removed by prolonged washing in water.

Plaster cements are used as the binding material in many artificial stones and imitation marbles, which are very suitable for interior decoration, but are of little use in situations exposed to the weather. The veinings of natural stone are imitated in various ways. A common method is to render plaster slow setting by gauging with size water, and to colour it by the addition of such substances as graphite, pyrolusite, cinnabar, litharge, chromium oxide, or zinc white. This mixture is then kneaded together on a glass plate so as to form a paste. For the preparation of **Marezzo marble,** fibrous materials dipped in a cream, or slip of Keene's cement (p. 125), coloured to the tint desired for the veining, are arranged on a glass plate. A thin coat of slip, tinted to the body colour of the marble, is then poured on the plate. The threads are picked out, leaving some of their coloured slip in the place they occupied, and dry Keene's cement is added to absorb the superfluous moisture. A backing of cement is then added to give rigidity to the slab.

According to Czermak (British Patent, No. 9,370, of 1901), marble may be copied in the following manner: A thin slip of coloured plaster is cast on a glass plate. The plaster is allowed to set and is then broken and the fragments separated slightly from each other. Plaster of another colour is then applied so as to fill up the interstices and produce veinings.

Scagliola is the trade name of a stone manufactured from Keene's cement mixed with colouring matters, to which is added water containing dissolved glue or isinglass.

Sorel cement is employed for the manufacture of stones of great mechanical strength. Particles of carborundum or corundum cemented with this material form abrasive wheels, but these are not of the best quality (see p. 455). Stone stairways and stair treads are prepared with sorel cement, and in some localities this material is used in the manufacture of building blocks and window sills. Unfortunately, it is not very resistant to the weather.

This cement is sometimes employed as the binding material for artificial marbles, as the cement sets to a hard mass capable of taking a very fine polish.

Other binding materials utilised in special cases for artificial stones are asphalt, pitch, wax, casein, powdered talc, sulphite cellulose, mica, and vermiculite. A stone may also be prepared by mixing sand with linseed oil and flowers of sulphur. On heating the mixture, vulcanisation takes place and a solid block is produced.

Moreau marble is prepared by immersing soft amorphous limestone in a bath of zinc sulphate so as to harden it. The limestone blocks are cut to size and stained before immersion. Afterwards they are dried by hot air, and in some cases the blocks themselves are heated.

The material has a crushing strength of over 4,000 lbs. per square inch and, on polishing, gives a surface equal to that produced on natural marble.

Sand-lime bricks (p. 239) are sometimes made in larger sizes, and the material is then classed as an artificial stone.

Blast furnace slag is cast in iron moulds and then allowed to cool slowly in an annealing oven. Bricks so produced make a good paving material. See also "Clinker Bricks" (*ante*).

Precast stone (see "Reconstructed stone").

Reconstructed stone is usually manufactured from quarry debris, which may consist of silica rock, limestone, granite, or other igneous rocks.

For many years numerous patents have been granted for various kinds of "reconstructed stone," but at the present time the term chiefly refers to various kinds of concrete in which Portland cement is the binding agent.

The following British Standard Specifications relate to articles made of concrete and other forms of reconstructed stone:—

No. 1217. Cast Stone (1945).
Nos. 492, 728, 834. Precast Concrete Blocks (1944).
No. 1234. Concrete Copings (1945).
No. 1237. Concrete Lintels (1945).
No. 1239. Concrete Lintels (1946).
No. 1289. Concrete Flue Blocks for Gas Fires.
No. 340. Precast Concrete Kerbs, Channels, and Quadrants (1936).
No. 492. Precast Concrete Partition Slabs (1944).
No. 368. Precast Concrete Flags (1936).
PD. 676. Precast Concrete Flags (1947).

SECTION LXII

SODIUM SILICATE, WATER-GLASS, SOLUBLE GLASS

BY JAMES SHELTON, F.I.C.

REVISED BY WILFRID FRANCIS

LITERATURE

J. G. VAIL (Philadelphia Quartz Co.).—"Soluble Silicates in Industry." Chemical Catalog Co. Inc., 1928.
HERMAN MAYER.—"Das Wasserglas, seine Eigenschaften, seine Herstelling und Verwendung." 2nd ed. Brunswick.
ULLMAN'S "Enzyklopädie der Technischen Chemie." Vol. 9. Berlin, 1932.
GMELIN'S "Handbuch der Anorganischen Chemie." Teil 21. Berlin, 1928.
J. R. PARTINGTON.—"The Alkali Industry." London, 1925.
R. N. SHREVE.—"Chemical Process Industries." New York, 1945.
R. C. MERRILL (Philadelphia Quartz Co.).—"Chemistry of the Soluble Silicates." *J. Chem. Educ.*, June 1947.
R. C. MERRILL.—"Industrial Applications of the Sodium Silicates." *Ind. Eng. Chem.*, **41**, 2, 337 (1949).

SOLUBLE sodium silicates are systems containing varying proportions of the alkali and silica (SiO_2), usually with at least some water. More than fifty products containing these three constituents are commercially available, and at least fifteen crystalline alkali metal silicates are known.

Although alkali and silica may be combined in all proportions, present commercial products do not exceed a silica to alkali ratio of about four to one because of the very low solubility of fused silicates above this ratio. By combining alkali, silica, and water in varying proportions a large number of different products with widely varying properties can be obtained. These range from readily soluble crystals to white powders which do not dissolve in boiling water, and from thin, slightly sticky fluids, to lumps of transparent glass which may have sharp edges.

A solution of sodium carbonate or hydroxide slowly dissolves silica. The rate of solution may be accelerated by boiling under pressure, and this is one of the methods employed for the manufacture of sodium silicate. Flint is commonly used as the source of silica; it is reduced to a fine state of subdivision by heating to redness, then quenched by tipping it into a large mass of water and grinding the cracked mass to a fine powder. In some districts infusorial earth is used instead of silica. The silica powder is digested with caustic soda in an iron boiler for about twelve hours at a pressure of about 60 lbs. per square inch. An almost neutral liquor is thus obtained, and this is concentrated until it has a specific gravity of about 1.7. The syrupy solution containing about 50 per cent. of sodium silicate is put on the market under the names **sodium silicate, water-glass, soluble glass,** etc.

Alternative Methods of Production.—According to Merrill (*loc. cit.*) at least six methods may be used to prepare the soluble silicates. They are manufactured in the United States at present almost exclusively by the fusion of sand and soda ash, in large open hearth furnaces, at temperatures around 1,300° C., according to the equation—

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O.nSiO_2 + CO_2$$

The most common commercial silicates correspond to values of n in the above equation equal to 2.0 and 3.2. Intermediate ratios may be made by mixing, and more alkaline grades by adding caustic soda. The reaction forming the most alkaline silicates can be completed below the fusion temperature of the mixture.

The more alkaline silicates may be made by fusing sand or a higher ratio silicate with sodium hydroxide. This reaction can also be completed below the fusion temperature.

In Europe, the soluble silicates are made using sulphate and coal in place of soda ash. The equation may be written—

$$2Na_2SO_4 + C + nSiO_2 \rightarrow 2Na_2O.nSiO_2 + 2SO_2 \uparrow + CO_2 \uparrow$$

The mechanism of this process is not known, although it is common knowledge in the industry that, due to side reactions, more coal is required than is indicated by this equation. In order to make sure that no coal remains in the product, an excess of sulphate is generally used. The product of this process is usually less pure than that made by soda ash fusion.

The soluble silicates may also be made by dissolving siliceous materials in concentrated caustic soda solution at elevated temperatures, usually under pressure. The reaction may be written—

$$nSiO_2 + 2NaOH \rightarrow Na_2O.nSiO_2 + H_2O$$

Powdered flint, infusorial earth, precipitated silica, or charred rice hulls (which contain about 35 per cent. silica) dissolve in 20 per cent. sodium hydroxide solution in about three hours, with agitation under three to four atmospheres pressure. Quartz takes longer to dissolve and requires a higher pressure. It is reported that silica dissolves more rapidly in potassium than sodium silicate solutions, and even faster in mixtures of the two.

The amount of silica which dissolves is apparently limited, although silica to alkali ratios as high as 2.7 have been reported in the literature. Ratios as high as 4.2 have been produced by electrolysing more alkaline silicates in a cell with a mercury cathode.

Silicon and its alloys, with iron or manganese, react with sodium hydroxide solutions, liberating hydrogen and forming sodium silicates. The reaction may be written—

$$Si + 2NaOH + H_2O \rightarrow Na_2O.SiO_2 + {}_2H_2 \uparrow$$

This **Jaubert** or **Silicol** process was used in Great Britain for a short time in World War I. but does not appear to be economical under present conditions.

A great deal of work has been done on the preparation of silicates directly from salt and sand by the reaction—

$$2NaCl + nSiO_2 + H_2O \rightarrow Na_2O.nSiO_2 + 2HCl$$

Silicate can be made by this method, but the reaction equilibrium apparently does not favour the production of silicate. For this reason, and because of the slow rate and low thermal efficiency involved in carrying out the reaction, it seems unlikely that silicates will be produced extensively on a commercial scale by this method.

Dissolving Silicate Glass.—The silicate produced by the soda ash fusion process forms, on cooling the melt, a clear light bluish-green glass. The colour is due to traces of iron or other impurities. In commercial sodium silicate glasses made in the United States the impurities amount to less than 1 per cent. Silicate glasses or powders with a silica to alkali ration of about 2.0 dissolve if finely ground. Those with a ratio above 2.5 do not dissolve when brought into contact with either cold or boiling water, although some alkali is leached out. The highly siliceous silicates must be dissolved by steam under pressure.

This process is usually carried out by the manufacturer and the solution sold in strength as concentrated as possible. The silicate with a silica to alkali ratio by weight of 3.2 can be handled readily only below concentrations of 40 per cent. solids, corresponding to a specific gravity of 1.41 or 43° Beaumé. The more alkaline silicates can be handled readily at higher concentrations. The 2.0 ratio silicate is frequently sold at a concentration of 54 per cent. solids, corresponding to a specific gravity of 1.69 or 60° Beaumé.

A recent process worked out for the preparation of a high $SiO_2.Na_2O$ solution, without the use of an autoclave, is described in the 3rd Annual Report of the East African Industrial Research Board for 1945. In this process, sand and soda ash were fused in proportions (actually about 1.7 molecular ratio) that would give a frit readily soluble in water at atmospheric pressure. To the boiling solution diatomite was added, and from it silica was dissolved. By this means stable silicate solutions were obtained with silica-soda ratios as high as 2.9. These results confirmed an observation made during the working-out of the wet process, *i.e.*, that the reaction proceeds in two distinct steps, viz. (1) the formation of a monosilicate, and (2) the formation of higher silicates. It was supposed that the monosilicate solution had the property of dissolving silica.

Properties and Uses.—Sodium silicate is decomposed by acids as weak as solutions of carbon dioxide, gelatinous silica being deposited, but, with bases such as lime and magnesia, insoluble silicates are produced. Because of these properties water-glass is largely employed as a cementing material and for reducing the porosity of stones. It is also employed as a rust-proof coating for metals, for the preparation of silicated soaps, for impregnating wood or cloth to reduce inflammability, and as a fixing agent for various dyes, especially in stereochromic work.

The following information on the utilisation of soluble silicates is abstracted from the excellent recent paper by Merrill (*loc. cit.*).

One of the largest uses for colloidal silicates of soda having a silica to alkali ratio of 2.8 to 3.9

is as adhesives for many types of materials, particularly paper-board used in the manufacture of corrugated containers. The present annual consumption in the United States for this purpose is about 400,000 tons of the commercial silicate solutions containing 32 to 47 per cent. solids.

Although the largest amounts of silicate used as adhesives are for bonding paper, they are also used for wood, metals, and other materials. Aluminium sheets, coated with silicate, may be bonded to cellulose. Acid-proof tanks are made by using silicate to hold fabric with a polyvinyl halide coating (which does not itself adhere well to metal) to a metal tank. Characteristics and a few applications of commercial grades of silicates at present most commonly used as adhesives are summarised in Table I.

TABLE I

CHARACTERISTICS OF SILICATES OF SODA USED AS ADHESIVES (Merrill)

Per cent. Na_2O.	Per cent. SiO_2.	SiO_2/Na_2O Wt. Ratio.	Sp.Gr. at 20° C., °Bé.	Viscosity at 20° C., Poises.	Uses.
11.0	31.9	2.9	47	9.6	Sealing cartons, shipping containers, metal foils, wall boards, flooring, and trunk making
8.9	28.7	3.2	41	1.8	Corrugated paper-board, flooring, paper tubes
9.2	29.5	3.2	42	4.0	Combined board (wall-board) plywood
8.3	28.2	3.4	39.7	3.3	Corrugated paper-board
6.7	25.3	3.7	35.0	2.2	Special uses

The loss of 1 or 2 per cent. of water from commercial adhesive silicates converts them from a liquid to an essentially solid material. This loss of water, either by evaporation or by absorption through the porous materials to be bonded, is the mechanism by which silicate adhesives "set." The rate of set at an equivalent viscosity increases with ratio of silica to alkali. Tackiness is greater for the more alkaline ratios. This fast setting is of particular value on corrugating machines, which have been successfully operated at speeds as high as 500 ft. per minute with a silicate adhesive and best modern techniques.

The advantage of a sodium silicate adhesive include good spreading and contact, a rate of set controllable over wide limits, and formation of a permanent strong, rigid, and heat-resistant bond. The quality of the silicate bond is not ordinarily affected by storage and its strength is greater than that of paper-board and other materials with which it is frequently used. The low price, uniform quality, controllable characteristics, convenience, and unattractiveness to animal life are also advantages.

Because of their alkalinity, silicate adhesives may attack the rosin size of paper and cause staining. This is frequently avoided by spreading a viscous silicate in a thin layer and drying rapidly. Another method is to pretreat the paper or other material with ammonium salts or metallic salts, such as zinc sulphate or magnesium chloride. Pretreatment with aluminium chloride not only prevents staining and desizing but also gives a waterproof bond. A laminated board made from plies, given this pretreatment, after 2.5 hours' immersion in water adsorbed only 35 per cent. water and gave a Mullen test of 247 as compared with 57 per cent. and 223 for the untreated board. Paper-board containers made by this process have met U.S. specifications covering a waterproof box for export.

Although not completely waterproof, silicate bonds show considerable resistance to moisture, which increases with age and ratio of silica to alkali. The water resistance may be improved by the addition of fine powders, such as zinc oxide, a silica gel-coated anhydrite, or whiting or other amorphous form of calcium carbonate, which react slowly with the silicate to form an insoluble mass. Up to 10 per cent. of zinc oxide may be dispersed in the silicate at 150°–180° C. to form an apparently homogeneous product. The addition to silicates of complex amine salts, formed by adding aqueous ammonia or amines to a zinc or copper salt solution, also improves their water resistance.

The flexibility of films from silicate adhesives may be improved by the addition of a small amount of coumarone-indene resin, sugars, molasses, starch, water soluble gums, glycerol, or rubber latex. Sorbitol and most other polyhydroxy derivatives are effective. Carboxymethylcellulose, sodium alginate, and a special oxidised cellulose have likewise proved satisfactory for this purpose.

Silicate-Clay Adhesives.—The addition of clay to a diluted silicate of soda increases viscosity but has a smaller effect on the rate of set. Mixtures containing large amounts of clay (up to 80 per cent.) have been used for many years in laminated paper products, such as wall board, because they have a lower setting time and a smaller alkali content than straight silicate adhesives. Such mixtures cannot be used on modern high-speed continuous pasting machines, which require faster and more accurately controlled setting. Recent tendencies to use more water-resistant paper stock also make it desirable to use an adhesive with increased wetting action, which retains the advantages of silicate-clay mixtures.

Modern silicate-clay adhesives, which accomplish these results, are prepared by adding a deflocculated clay slip, prepared by mixing with a 0.1 to 0.5 per cent. solution of a dispersing agent, to a concentrated sodium silicate having a silica to alkali ratio of 2.5.

The usual clay content of a modern adhesive of this type is from 6 to 20 per cent. The clay may also be dispersed by mixing with the silicate at 115°–162° C. at 10 to 80 lbs. per square inch pressure, or by passing the mixture through a colloid mill.

One main advantage of modern clay-silicate adhesives is that their controllable thixotropic character and lower water content per unit area of board give faster, readily controlled setting, permitting increased machine speeds and decreased heating and seasoning or storage time. They spread well, even on highly sized or water-resistant boards, and give a strong bond with little penetration into the paper. Under the same plant conditions, 11 to 12 lbs. per square foot of a silicate-clay adhesive are used per 1,000 square feet as compared with 17 lbs. for the straight silicate.

Soap Builders.—Although sodium silicates were added to soaps on a fairly extensive scale as early as 1937, only within the past twenty-five years has it become recognised and established by both laboratory studies and practical experience that silicates, as well as soaps, are good detergents, and that a mixture of the two is often better for many cleaning purposes. The use of sodium silicates to produce a good soap is of particular importance during periods when fats and oils for soap-making are scarce.

Metal Cleaning.—Because of their detergent properties, together with comparative freedom from attack on most metals, even those sensitive to alkalies, silicates are used in many metal cleaning operations. The protective action of the silica or silicate ions is apparently due to an invisible film of silica, or metal silicate, which does not interfere with electroplating. The film formed on steel during cathodic cleaning in sodium metasilicate solutions is claimed, on the basis of electron diffraction patterns, to be a complex ferroferrisilicate ($9FeO.Fe_2O_3.3SiO_2.8H_2O$).

Because the metasilicate attacks aluminium only below a concentration of 0.6 per cent., and silicates with a silica to alkali ratio greater than 2.0 do not attack the metal, a mixture of sodium metasilicate and a more siliceous silicate is used for aluminium cleaning.

Cements.—A variety of cements is made with powders and solutions of silicates of sodium and potassium of widely varying silica to alkali ratios. These are used for acid-proof construction, digester linings, mending broken saggars in potteries, lining and coating refractories, and lining crucibles, brass furnaces, ladles, sulphite digesters for chemical wood pulp, and other similar units. Chimney, coke oven, stove, furnace, tunnel, spark plug, and patching cements are made with silicates of soda. Suitable mixtures have also been developed for binding porcelain and glass to metal and china to glass.

The advantages of silicates as binders include resistance to acids (with the single exception of hydrofluoric acid and some of its derivatives), ability to withstand high temperature, ease of application, low price, resistance to water when dehydrated, and strong bonding action to many types of surfaces both by air drying and on heating. Setting may occur by loss of moisture, or by the formation of a silica gel or heavy metal silicate.

Briquettes and Bonded Materials.—The adhesive character and low cost of silicates of soda cause their use in bonding a variety of materials, including coal. Only recently has coal briquetting with silicate been successful on a commercial scale. Difficulties were that the silicate coating was partially water soluble and that the silicate acted as a flux for the ash, forming slag which deposited on the grates of the furnace. A method of overcoming this difficulty is to add a material, such as calcium carbonate, or some clay which reacts with silicate, to form a product with a high fusion point.

During the war, three processes were developed in France for the production of coal-dust briquettes, using silicate to replace and extend pitch. Two involved the preparation of an emulsion or paste of a 3.5 ratio silicate solution with pitch. The third method used a powdered disilicate glass. The silicate consumption for this purpose grew to 35,000 tons in three years, or 53.7 per cent. of the sodium silicates consumed in France that year. The amount used per ton of briquettes decreased from 10.3 per cent. in 1941 to 4.4 per cent. in 1943.

Abrasive wheels are made by bonding the abrasive grains with a 2.0 ratio silicate, usually in combination with clay, and sometimes with a small amount of zinc oxide for water resistance. Similar mixtures are used for grinding and polishing wheel cements, although these frequently contain a less alkaline silicate, and several additives.

Other Uses.—Although the above uses now consume a major share of the sodium silicates produced, these are not all of the commercial applications. Another large group of uses involves the reaction of sodium silicates with acids, sodium aluminate, and other materials to form catalyst, desiccant, and base-exchange gels. Silicates of soda are used in roofing, granules, coatings, sizings, and paints as deflocculants, and in flotation reagents.

According to the U.S. Bureau of the Census, the production of all forms of sodium silicate in the U.S. during 1947 was 474,589 tons, calculated on an anhydrous basis, corresponding to about 1,500,000 tons of the commercial solutions or "liquid" silicates.

SECTION LXIII

LUTES AND MISCELLANEOUS CEMENTS

By Geoffrey Martin, Ph.D., D.Sc.

LITERATURE

H. Bennett.—"The Chemical Formulary." New York, 1950.

R. C. Merrill.—"Industrial Applications of the Sodium Silicates." *Ind. Eng. Chem.* 41, 2, 337 (1949).

Lafarge Aluminous Cement Co. Ltd.—"Refractory Concrete." London, 1949.

The more important cements have been described above in the preceding articles. There remain, however, a considerable number of miscellaneous lutes and cements which are of the greatest possible use to the chemical engineer and works chemist, and a brief account of these will not be out of place here.

Lutes and Cements to Resist Sulphuric and Nitric Acids.—(1) Powdered pumice is mixed with silicate of soda solution of 50° Bé. If the lute is required to set hard add a base like red lead, or lime, or magnesium oxide.

(2) A mixture is made of 2 parts of powdered asbestos, 1 part of barium sulphate, and 2 parts of silicate of soda solution of 50° Bé. density if the acids acting on the surface are concentrated, and 130° Bé. if they are dilute. In any case the surface of the cement should be painted with acids.

Another good lute much used for **nitric acid retorts** consists of blue asbestos fibres, blue asbestos powder, sodium silicate solution, together with a little tallow and boiled linseed oil.

(3) A cement which will resist hot nitric acid consists of a mixture of 1 part of asbestos, 1 part of sand, and 2 parts of silicate of soda.

(4) Acid pipes are usually luted with wet blue asbestos fibres, pressed together so as to form a paste or mat, and moistened with sodium silicate solution.

Lute Proof against Nitric and Hydrochloric Acid Vapour.—Mix together 1 part resin, 1 part sulphur, 2 parts brick dust. Then melt together.

Lutes for Chemical Retorts.—(1) The following is a very ancient one:—Mix together 2 parts of fine lime, 2 parts of fine flour, and 1 part of potter's earth. Beat up the white of egg with an equal bulk of water, and make the solids into a paste with the liquid.

(2) A well-known recipe, which is also used in melting pots, is this:—Mix sifted brick dust with an equal amount of red lead. Rub the mixture with boiled linseed oil and coarse sand to the stiffness of cement. To cover vessels, apply the paste and then dust sand over it.

(3) For large pots use a mixture of 3 parts litharge, 2 parts freshly burnt pulverised lime, 1 part white bole; linseed oil.

(4) Freshly slaked lime is mixed into a concentrated solution of borax. The mixture is applied with a stiff brush and allowed to dry. When heated the cement fuses to a glaze.

See also above under "Lutes and Cements to resist Nitric and Sulphuric Acids."

Crucible Lutes.—(1) Powdered clay and brick dust are mixed with a solution of borax in water.

(2) Freshly slaked lime and a concentrated solution of borax are made into a paste and allowed to thoroughly dry after applying.

Crucible Cements.—(1) Mix powdered clay and brick dust with water or a solution of borax. With the borax the lute fuses to a compact vitreous mass in the crucible.

(2) 2 parts slaked lime, 2 parts borax, and 1 part of litharge and water are made into a paste.

Cement for Furnaces.—Fire-clay, 1 part; burnt fire-clay, 1 part; mixed with sufficient silica of soda to make it plastic. A large number of cements for furnaces is now available under various trade names. See under "Refractory Cements" (p. 138 and 233).

Cement to Resist White Heat.—Plumbago, 1 part; manganese dioxide, 1 part; salt, ½ part; borax, ½ part; iron filings, free from iron oxide, 2 parts; pulverised clay, 4 parts. Mix with water to form a thick paste; use immediately, and heat slowly to nearly whiteness.

Water-Glass, Zinc, and Pyrolusite Cement.—Mix quickly together 100 parts zinc white, 80 parts pyrolusite, 20 parts water-glass and apply at once. This cement hardens in a short time, and is adapted for cementing the joints of pipes exposed to red heat. When fused it forms a glass-like joint of great adhesive power.

A joint which will resist moderate heat is made by mixing asbestos powder into a thick paste with liquid silicate of soda.

Non-conducting Cement for Covering Boilers and Steam-Pipes.—Mix together Portland cement, 1 part; flour, 2 parts; sawdust, 4 parts; fine sand, 1 part. Next mix in clay, 4 parts; plasterer's hair, ½ part. Mix well with water to consistency of mortar, and apply with a trowel to the thickness of 1 in. When dry apply successive coats of 1 in. thickness until a depth of 5-7 in. thickness of composition is applied. Each coat must be dry before the next is applied. Finally, give two to three coats of tar.

Many such compositions are sold, the main basis being asbestos.

Cement for Fixing Tiles in Fireplaces and Grates.—Mix equal parts of plaster of Paris, sand, and hair mortar.

Cement for Fixing Iron Bars into Stone.—Use a compound of equal parts of pitch and sulphur.

Cement for Seams and Joints of Stone Cisterns.—Use 6 parts of powdered brick; 1 part of white lead; 1 part of litharge. Mix to a paste with boiled linseed oil.

Cement for Steam and Water Joints.—(1) Powdered litharge, 10 lbs.; plaster of Paris, 4 lbs.; red lead, 2 lbs.; yellow ochre, ½ lb.; hemp cut into ½-in. lengths, ½ oz. Mix with boiled linseed oil to consistency of putty.

(2) White lead, 10 parts; manganese dioxide, 3 parts; litharge, 1 part. Mix to a putty with boiled linseed oil.

(3) The following is a good cement for faced steam joints:—White lead, 1 part; red lead, 1 part. Mix with linseed oil to a putty. When great heat has to be resisted add 1 part of plumbago to above mixture.

Cement for Cisterns and Watercourses.—Mix together powdered burnt clay, 50 parts; powdered fire-brick, 40 parts; litharge, 10 parts. Stir in boiled linseed oil until the mass becomes of the consistency of a paste. Wet with water the parts to be covered before applying.

Rust Joint Cement for Cast-Iron Cisterns.—(1) Cast-iron borings, 5 lbs.; powdered sal ammoniac, 1 oz.; flour of sulphur, 2 oz. Mix with water.

(2) A slower acting but better cement consists of cast-iron borings, 6 lbs.; powdered sal ammoniac, 1 oz.; flour of sulphur, ½ oz. Mix with water.

The weight in pounds of dry iron borings to be used in making a joint is obtained by dividing by five the cubic contents in inches of the joint.

(3) Another much used mixture consists of iron filings, sal ammoniac, and acetic acid. Used for joining together the sections of cast-iron nitric acid stills.

Enamel Glaze Cement for Coating Iron Pans.—Flint glass, 130 parts; sodium carbonate, 20.5 parts; boric acid, 12 parts. First dry at 100° C., then heat to redness, and carefully anneal.

Cement for Marble.—(1) Fine sand, 20; litharge, 2; dry slaked lime, 1; plaster of Paris, 1. Make into a putty with boiled linseed oil.

(2) **Keene's Marble Cement** consists of baked plaster of Paris, moistened with a saturated solution of alum, recalcined and reduced to powder.

Cements for Joining Metals and Woods.—(1) Melt resin and stir into it calcined plaster of Paris until the mass is pasty. Add boiled oil until the paste is thinned somewhat, and apply hot.

(2) Dissolve in boiling water, glue, 2¼ lbs.; gum ammoniacum, 2 oz. Add in small quantities 2 oz. sulphuric acid.

Cements for Joining Metals to Earthenware.—Mix together washed fine sand, 20 parts; litharge, 2 parts; powdered quicklime, 1 part; mix with boiled linseed oil, and colour with pigments.

Cements for Joining Metals to Glass.—(1) Mix 2 parts of powdered litharge and 1 part of white lead. Then stir this powder into the liquid formed by mixing 3 parts boiled linseed oil with 1 part of copal varnish.

(2) Melt together with stirring on the water bath, copal varnish, 15; drying oil, 5; turpentine, 3. Then add 10 parts slaked lime.

Turner's Cement.—Bees' wax, 2 parts; resin, 1 part; pitch, 1 part. Melt together and stir in fine brick dust.

Cement for Plumbers.—Black resin, 1 part; brick dust, 2 parts. Melt together.

Cement for Joining Porcelain Heads to Metal Bars.—Mix Portland cement with hot glue.

Cement for Fixing Pyrometers into Furnaces.—A mixture of litharge and glycerine is much used.

Composition Insoluble in Benzene and Petroleum.—Gelatine mixed with glycerine yields a liquid when hot, but which solidifies on cooling, forming a tough elastic material which much resembles indiarubber, and is quite insoluble in petroleum or benzene.

Casks can be made impervious to benzene or petroleum by painting on the inside with this compound.

The material is also used for printers' rollers, and also buffers for stamps.

It should be noted that ordinary **soap** is insoluble in benzene, and forms a good lute. Therefore also a good lubricant for pumps working benzene, and for threads of screws.

Joints which will resist benzene may be made of a mixture of plaster of Paris and hot liquefied glue. Apply hot. Litharge and glycerine also form a good lute.

Lute for Neck of Bottles with Glass Stoppers.—Take equal parts of linseed meal and whiting, and make into a stiff paste with water. Apply round stopper.

Dental Cements.—(1) 1 part of finest pulverised glass is mixed with 3 parts of calcined zinc oxide (which must be kept in well-stoppered bottles). 1 part of borax is dissolved in the minimum amount of water, and mixed with zinc chloride solution of 1.5 sp. gr., which must also be kept in a well corked bottle. For use, the powder is mixed with some of the liquid to form a putty, which soon hardens to a stone-like mass. The material is an excellent, tenacious, quick-binding cement.

(2) 5 parts of oxide of zinc, 2 parts silica (silex), 1 part borax, are moistened with a solution of 1 oz. zinc chloride in 6 drachms water. It sets in thirty minutes.

Refractory Cements.—Silicate of soda refractory cements are made by mixing refractory fillers with silicate solutions to form plastic mixtures. Dry cements are made by mixing fillers with powdered silicates and adding water just before use. Filler materials in regular use include raw and burned fire-clay, ground fire-bricks, various forms of silica (sand, ground quartz, and ganister), chromite, ground mica, asbestos, graphite, periclase, soapstone, and artificial refractory materials, such as silicon carbide fire-sand. Pyrophyllite, forsterite, and crushed olivine are recommended as fillers for refractory cements.

Best results are obtained with mixtures of two or more of these ingredients, and several sizes of particles. The heat resistance of a silicate cement is much greater than that of the silicate itself.

Refractory cements, patching compounds, and furnace linings can also be made by mixing ciment fondu with grogs of highly refractory compounds, such as fire-brick, chrome, magnesia, alumina, or zirconia. For further details see Section LIX. and the publications by the Lafarge Aluminous Cement Co. mentioned in the literature.

The following acid-proof cements are given in *C.I.O.S.* Report, Item No. 22:—

Acid-proof Cements:

	Composition.	Formulation.	Properties resistant to	Uses.
S W 10 and 20	4.0 Na_2SiF_6 2.0 Clay 94.0 Quartz	Mix with sod. sil. containing 8 per cent. Na_2O and 26 per cent. SiO_2	All acids except HF and H_2SO_4	Acid-proof brick linings; not liquid tight
S W K	6.0 K_2SiF_6 3.0 Sol. H_2SiO_3 2.0 Clay 89.0 SiO_2	Pot. sil. solution containing 10 per cent. K_2O and 23.5 per cent. SiO_2	H_2SO_4, all concentrated	Masonry; joints
S W D — Z	4.0 Na_2SiF_6 2.0 K_2SiF_6 0.8 $CaSiF_6$ 5.2 Clay 3.2 H_2SiO_3 1.5 $CaSO_4$ 20.0 slag wool powder 63.3 SiO_2 sand	Sod. sil. containing 11.6 per cent. Na_2O and 31.5 per cent. SiO_2	Especially resistant to H_2SO_3	Ceramic linings for pressure vessels, *e.g.*, cellulose digesters
K refractory cement	3.0 K_2SiF_6 12.0 $BaSO_4$ 3.0 Sol.H_2SiO_3 50.0 fire-brick powder 32.0 SiO_2 powder	Pot. sil. solution containing 10.5 per cent. K_2O and 23.5 per cent. SiO_2	All except HF	Acid-proof and fire-proof masonry
Z acid-proof mortar	Na_2O 20.0 SiO_2 53.0 H_2O 27.0	79 parts H_2O to 21 parts powder	All except HF and H_2SO_4	Masonry and tile jointings

SECTION LXIV

CLAYS AND ALLIED MATERIALS

By Alfred B. Searle
Consulting Technologist

LITERATURE

A. B. Searle.—"British Clays, Shales, and Sands." 1912.
—— "The Natural History of Clay." 1912.
—— "The Clayworker's Handbook." 1949.
—— "The Chemistry and Physics of Clays and other Ceramic Materials." 1933.
—— "An Encyclopædia of Clays and other Ceramic Materials." 1931.
E. Bourry (translated and revised by A. B. Searle).—"Treatise on Ceramic Industries." 1926.
H. Ries.—"Clays: their Occurrence and Use," 1927.
Bruno Kerl.—"Handbuch der gesammten Tonindustrie." 1907.
H. Seger.—"Gesammelte Schriften." 1908.
G. R. Rigby.—"Mineralogy of Ceramic Materials". 1948.
The Transactions of the British Ceramic Society, *the British Clayworker*, *Claycraft* and *Ceramics*, as well as several American periodicals, frequently contain articles on Clays and allied materials.
The British Ceramic Research Association (Penkhull, Stoke-on-Trent) publishes frequent Bulletins containing the results of researches.

Most books on applied geology also deal with clays, though usually in a somewhat superficial manner. Further information on clays will be found in the literature listed under such headings as Pottery, Earthenware, Porcelain, Bricks, Tiles, Furnace Linings, and Refractory Materials in the present volume.

Patents.—There are many patents connected with the uses of clays and clay-products.

Geologically, clays are regarded as a product of the decomposition of granitic (felspathic) rocks, but the term is also applied to most minerals which possess the property of being plastic when mixed with a suitable amount of water. The materials included as "clays" by geologists, therefore, comprise many mixtures of clays and other minerals, and no classification of clays from the geological point of view is wholly satisfactory to those engaged in the industries in which clays are used.

So far as their **chemical constitution** is understood, clays appear to consist essentially of one or more aluminosilicic oxides, *i.e.* complex oxides containing silica and alumina combined with the elements of water, the whole forming a definite chemical compound series of 5 (**clay-minerals**).

For many years it has been understood that there is in all clays a certain essential and characteristic material—for which the term "clay substance" is usually employed, but a careful study of the products obtained by purifying various natural clays inevitably leads to the conclusion that the term "clay substance" is not one single chemical compound, but is applicable to a number of different substances, all of which are very closely related to each other. Just as in organic chemistry there is a large class of alcohols (ranging from the simple methyl alcohol to the highly complex sugars and benzene derivatives), so the term "clay substance" covers an enormous number of different substances of the same general properties and closely allied to each other, their chief characteristic being that they are aluminosilicic oxides. It should, however, be observed that the term "clay substance" is used somewhat loosely by some writers, and is often applied to crude clays which cannot be further purified than by the elutriation they have received. Such clays not infrequently contain a considerable proportion of rock flour of a highly siliceous or ferruginous character, together with extremely fine particles of mica and other minerals, which are clearly not of the nature of clay.

Chiefly as a result of the examination of X-ray spectographs and the time-temperature graphs produced when clays are heated at a uniform rate, there are certain clearly recognised **clay minerals**, the most important of which are kaolinite, montmorillonite, illite and attapulgite, with baddelite, beidelite, halloysite, dickite, nacrite, and nontronite as of minor importance.

Kaolinite = Al_2O_3, $2SiO_2$, $2H_2O$.—decomposes at 610° C.
Halloysite = Al_2O_3, $2SiO_2$, nH_2O.—decomposes at 310° C.
Montmorillonite = MgO, Al_2O_3, $5SiO_2.nH_2O$.—decomposes at about 875° C.
Attapulgite = $(OH_2)_4$, $(OH)_2$, Mg_5, Si_8O_{20}, $4H_2O$.—loses half water at 150° C.
Illite = $2K_2O$, 3(Mg Fe)O, 8(Al Fe)$_2$ O_3, $24SiO_2$, $12H_2O$.—decomposes at about 140° C.

These clay minerals are composed of atoms arranged in sheets, *e.g.*, kaolinite (the chief constituent of china clay) consists of sheets of six oxygen atoms, six silicon atoms, four oxygen and two hydroxal groups, four aluminium atoms and six hydroxyl groups. The silicon and aluminium atoms are so small in proportion to the oxygen atoms and the hydroxyl groups that they fit readily into the spaces between the latter. The thicknesses of the various unit sheets are: Kaolinite 7.2 Å, Halloysite 10.25 Å, Montmorillonite 9.2–21.4 Å, and Attapulgite *c.* 10.0 Å.[1]

In these sheets, each silica atom is always surrounded by four oxygen atoms forming a tetrahedral group. Each oxygen may be linked to either one silicon or may be common to two SiO_4 groups.

In all these minerals iron or magnesium atoms may replace aluminium, and iron atoms may replace silica.

The attachment of cations (*i.e.*, substances which form bases) to clay minerals is much looser than in simpler chemical compounds and replacements are common.

The readiness with which clay minerals can replace cations by hydrogen, and vice versa, causes important **exchange phenomena** and explains many properties of clays, including the power to adsorb certain dyes, to bleach oils, and either to remain in suspension or to flocculate.

The behaviour of clay minerals when heated is peculiar. Kaolinite decomposes at 610° C., halloysite at about 310° C., and montmorillonite at about 875° C., with evolution of water in each case. The resulting product appears to be a mixture of alumina and silica, both of which are highly refractory oxides, so that clay minerals do not show signs of fusion below 1,600°–1,700° C. Between the temperature at which the clay minerals decompose and that at which the product melts, several other changes in crystalline form occur, according to the temperature attained and the duration of the heating. Small proportions of impurities can greatly reduce the melting point of clay minerals. If the heating is sufficiently prolonged at a temperature above about 1,300° C. the free alumina will combine with some of the free silica and form another compound, **mullite** ($3Al_2O_3.2SiO_2$), which was, at one time, thought to be sillimanite (Al_2O_3, SiO_2).

Natural Clays are seldom pure and their purification is usually very difficult. The coarser particles of impurities can be removed by elutriation or by fractional sedimentation from suspension in water, preferably with the addition of a little ammonia, but the finer particles so obtained will contain a large proportion of rock flour, silica being the chief constituent. Separation by "heavy fluids" is of little help as the difference between the specific gravity of the clay minerals and the impurities is usually too small.

Much information may be obtained by examining the finer particles (which may be obtained by elutriation and contain all the true clay) by the following means:—

(i) X-ray spectrography;
(ii) Differential thermal graphs based on the changes in temperature of the material when heated in a steady rising temperature;
(iii) The electron microscope (which shows the shape of the particles);
(iv) Microscopic examination, including refractive index, birefringence, and optical extinction angles.

Purification of Clays. The only effective means of purifying clays commercially (and that is only partial) is by elutriation, which may be aided by the addition of small quantities of alkali. The separation of clays by means of an electric current (electro-osmosis) is sometimes practicable though expensive.

Chemical reagents will not remove these adventitious minerals, which occur in all clays in their natural condition, without simultaneously attacking the clay, nor is any solvent for the clay known which does not either decompose it or attack the impurities present in it. The usual methods of purification by crystallisation are inapplicable, and the formation of soluble or insoluble compounds which can afterwards be reconverted into the original clay has not yet been accomplished. Several investigators have attempted this method of purification, only to find that the clay itself was converted into simpler compounds from which the original substance could not be obtained.

---

[1] **Kaolinite** and **halloysite** are the chief constituents of china clay and some fire-clays and closely resemble each other. **Montmorillonite** is the chief clay mineral in **bentonite** and in some **fuller's earth**; it resembles the amphibole minerals. **Illite** is related to the micas and occurs in many shales.

It was formerly thought that clay minerals were acids because, when heated with a base or alkali they formed compounds. Theses minerals, when heated, decompose and the final product is a **mixture** of several compounds (silicates and aluminates) and not a single compound. It is now known that, on heating, the clay minerals form free alumina, free silica and water and that it is these free oxides which combine with the base or alkali to form a mixture of salts.

When very small proportions of alkali or base is added to a clay mineral in suspension in water a marked change in the nature of the suspension occurs. Alkalis usually increase the amount of clay still in suspension after a long period of standing; acids tend to cause flocculation and rapid deposition of some or all the clay. These changes are allied to the base-exchange properties in the clay (p. 140).

When heated for a long time with concentrated sulphuric acid, clays are converted into soluble aluminium sulphate and silicic acid, silica, or silica and alumina. Unfortunately, this treatment cannot be made the basis of a method of determining the proportion of true clay in a sample, though it has been erroneously used for this purpose ever since Seger's classical research on the subject more than forty years ago; with very pure clays—such as the finest grades of kaolin or china clay—fairly consistent results are obtained, but even these usually show a larger proportion of free silica than is actually present, and the method is therefore liable to be seriously misleading.

Colloidal Properties.—Although under the microscope and in X-ray spectrographs clays are found to consist essentially of crystalline particles, most clays, when mixed with sufficient water, behave as colloidal materials. These are, like colloids, very sensitive to the addition of very small quantities of acids and alkalis, they readily form colloidal suspensions (*sols*) and colloidal solids (*gels*), and much use is made of these colloidal properties (see p. 142).

The **plasticity** of clays is almost as complex as their constitution, and though many theories have been published concerning the cause of it, none of them are entirely satisfactory.

That plasticity is an inherent property of the clay molecule, connected with its sheet-like structure, seems to be unquestionable, though the production of some amount of plasticity (or what is regarded as such) in very fine powders of various substances seems to throw some doubt on the statement just made. When an attempt is made to define plasticity in such terms as will render its measurement possible, it is soon found that this property is not of an elementary nature, but that it unites within itself such properties as cohesion, adhesion, elasticity, tensile strength, etc., and that any basis of measurement of the plasticity of a clay paste must include all these properties, and possibly some others. For this reason, any attempt to measure plasticity in terms of water or dyes absorbed, tensile strength, or linear extension when subjected to measured tensions, must prove incomplete, and the suggestion of Zschokke, amplified by Rasenow, to express plasticity in terms of the water required, multiplied by the percentage of linear extension, and the product multiplied by the tensile strength, is by no means as reliable as is desirable. At the same time it forms the best means of measuring the plasticity hitherto suggested. The suggestion of Ashley, that the plasticity of clay may be expressed in terms of the percentage of dye adsorbed, does not place a series of clays in the same order of relative plasticity as would agree with the experience of practical potters, and appears to be unreliable.

The most generally accepted view of the plasticity of clay is that the sheets of atoms which form the units of clay minerals are capable of holding relatively large volumes of water, which impart mobility to the mass and so enable it readily to change its shape under pressure and yet permit it (when the quantity of water is not excessive) to retain the new shape when pressure has been removed. Some clays are rendered plastic by admixture with oil, but most organic fluids do not possess this property.

Bingham has suggested that plasticity may be measured by plotting the rate of extrusion against the pressure applied. With Newtonian liquids the resulting graph is a straight line starting from zero and corresponds to the viscosity of a fluid; with non-Newtonian fluids the graph is a curved line. With plastic clays there is no flow until a critical pressure is reached, after which the clay behaves like a Newtonian fluid. On projecting the sloping line to the base, a distance from the zero to the point of contact corresponds to the **yield value** which bears some relation to the plasticity of many clays. Clays with a high yield value are too stiff to work satisfactorily; those with a very low value are too soft and sticky. The yield values of clay pastes of good workable consistency lie between 2,000 and 10,000 dynes per cm^3. The addition of small quantities of sodium silicate or sodium carbonate reduces the yield value and make the paste more fluid.

Apart from all questions of measurement, plasticity may be defined as that inherent force which permits a substance to be altered in shape with the application of only a small force, the new shape being retained when the force no longer acts upon the material. In practice, an experienced potter, or other clayworker, will ascertain the relative plasticity of a number of clays by "feeling" them, but this method does not appear to be susceptible of accurate measurement.

The various theories relating to plasticity, together with much other information on this very interesting property of clays, will be found in some of the books mentioned in the list on p. 149.

The **shrinkage** which articles made of clay paste undergo when dried is another characteristic property of most clays.

When a highly plastic clay is moulded and allowed to dry, the shrinkage is often so great that the piece is unable to withstand the internal strains produced and cracks into a number of smaller pieces. In very pronounced cases it may fall to a powdery mass. If the drying be carried out rapidly (especially with the aid of heat) the strains will be all the more intense, and it will be impossible to keep the goods whole. If, on the contrary, the drying is effected with extreme slowness, and care is taken to avoid irregular drying and draughts, it will not be difficult to obtain sound goods. The slow drying and the accompanying precautions are, however, so tedious as to make such "tender" clays of little commercial value, unless they can be treated with some non-plastic material. Thus, the addition of sand before making the clay into a paste, will reduce its tendency to shrink, and will consequently stop the cracking and disintegration. There is a limit to the proportion of sand which can be added; this limit is characteristic of each individual clay, and must therefore be ascertained by actual trial. There are large areas of valuable brick clays in the South of England which are quite useless commercially, because they are too plastic, and shrink too much. If sand could be added to them in reasonable proportions, such clays would be very useful, but the absence of sand in the localities in which these clays occur, and the cost of taking it to them being prohibitive, the clays must remain unused until some other practical method of reducing shrinkage has been found. Heating clay to a temperature of 600° C., before moulding will effect a result similar to that of adding sand, but the cost of this treatment is prohibitive for ordinary brick and tile clays.

Most colloidal substances have a characteristic shrinkage, and there is good reason to suppose that the suggestion of Schloesing—revived more recently by Rohland—that clays contain considerable proportions of colloidal matter is correct. At the same time, the constitution of clays is such that it is impossible to be certain about this, as the evidence of a colloidal structure is far from complete, and may be capable of quite a different interpretation.

What appears to take place in the drying of a plastic clay is that the particles are at first separated by a film of water; as this evaporates, the particles draw closer to each other until they are in intimate contact. This may occur before all the water has been evaporated, for there are still some pores in the mass even when the particles are as close together as they can be.

If clay is a colloidal material, a somewhat different explanation may be given; all colloids swell when exposed to water, and absorb a considerable quantity of it in the process. The action of dry glue when soaked in water is typical. On again drying the swollen colloidal mass, the water evaporates, and the solid particles draw nearer together, until finally a hard dry substance is produced. As colloids, like clays, appear to be complexes of very high molecular weight, the relationship between the two is interesting in many ways.

The practical difficulties which arise in the manipulation of clays in consequence of the shrinkage are numerous and complicated; they are described in the works named on p. 149.

The **impurities** in clays are chiefly of a mineral character and are due to the origin of the clay.

As already stated, clays are primarily formed by the decomposition of felspar and other alumino-silicates and are associated with numerous other minerals. The remarkable smallness of the particles of clay soon causes them to be removed by the action of water, and as the stream enters a lake, or has its speed of flow reduced by some other means, the clay particles are deposited and a secondary clay is formed. Some clays have been gathered up by water and deposited again and again, and are now found many miles from the place of their original formation.

In the course of their travels clays may become associated with many kinds of mineral and vegetable impurities, the most important of which are stones, sand, rock flour and silt, and vegetable matter derived from living or decomposed plants. The coarser particles may be separated by washing in a slow stream of water as already described, but the finest particles and much of the matter of vegetable origin cannot be removed in this way, but must enter into the composition of the material of which the bricks, pots, or other goods are made. The organic (vegetable) matter is removed when the goods are burned in the kiln, but its presence in the earlier stages of the burning often has a marked effect on the colour of the goods, as it exercises a strong reducing action on some of the oxides to which the clays owe their colour.

A process invented by Graf von Schwerin for the purification of clays consists in the subjection of a clay–slip to the action of an electric current. Many of these impurities remain behind, whilst the purified clay collects in a sheet at the cathode and is removed by a scraper. This method has been "pushed" vigorously, but has not proved sufficiently attractive in practice for many well-known firms to adopt it. Moreover, its limitations are very great and preclude its use in many cases. More recently, the addition of ammonia, or some other electrolyte, followed by a process of centrifugal grading has been successful.

To describe the effects of all the impurities in clays would necessitate a small volume, and as they have been dealt with in some of the volumes mentioned on p. 149, there is no need to do more than indicate the most important ones very briefly here.

Impurities containing soda, potash, lime, magnesia, or other similar oxides or carbonates combine with the clay at temperatures above 700° C. and produce aluminates and silicates more readily fusible than the clay itself. Hence, if a clay containing these impurities is heated sufficiently, a temperature will be reached at which some fusion will occur, the fused mass filling up some of the pores in the material. As the mass cools it will be found to be much stronger than if it had not been heated so intensely, for the fused, glassy matter will have bound the other particles together with great firmness. If the heating be continued at a still higher temperature, a point will be reached at which the mass has undergone so much fusion as to begin to lose its shape; this is the point of maximum practicable strength, or, as it is usually termed, the point of softening (vitrification). It is a point aimed at, but purposely never reached, by makers of engineering bricks, porcelain, and other impervious ware. If the heating is carried beyond this point distortion of the whole mass occurs and the articles are irretrievably spoiled. Any substance which facilitates this fusion is termed a **flux,** and as this property is possessed by most metallic oxides and carbonates, and by many sulphates and chlorides, a large number of the impurities in clay are fluxes.

Limestone is an impurity which is very common in boulder clays, and its presence is very inconvenient, especially in the manufacture of bricks. The difficulties caused by it may, however, be overcome by fine grinding and burning at a proper temperature. **Chalk,** on the contrary, is often added to clay to reduce the shrinkage and to increase the binding power.

Sand is a convenient term which includes all small mineral particles, no matter what their composition. Hence the action of sand on clay is complex. Fortunately, most sands are composed chiefly of silica, and may largely be regarded as impure forms of this oxide. The first action of sand on clay is to reduce its plasticity and shrinkage, and its presence is therefore a desideratum in many cases.

If coarse, sand prevents the clay from being used for work requiring a very fine finish, but this coarse sand can usually be removed by treating the clay in a wash mill. In the kiln, the sand may combine with some of the fluxes previously mentioned, and as simple silicates are usually more fusible than the more complex ones, the presence of sand may bring about an early vitrification of the material, and give it an undesirably low fusing point. At the same time, sand is, of itself, a refractory material, though not so resistant as pure clay, and the addition of it to a fusible clay will increase the heat resistance of the latter. On the other hand, the addition of sand to a pure clay will lower the fusing point of the clay.

The **metallic oxides and silicates** contained in clays in the form of sand or rock dust behave like the impurities just mentioned, and reduce the shrinkage and the resistance of the material to heat. At the same time they may determine the colour of the burned material.

Thus, clays containing more than 5 per cent. of iron oxide or its equivalent will usually burn red, but if reducing conditions prevail in the kiln, a dark grey (technically regarded as "blue") or a black mass will be produced from such clays. The action of each of the metallic oxides and silicates cannot be described here. Readers desiring it will find further information in the books mentioned on p. 149.

CLAYS OF COMMERCIAL IMPORTANCE

The following clays are of considerable technical importance. More information concerning them, together with a more complete list of valuable clays, is given in "British Clays, Shales, and Sands," by A. B. Searle.

Adobe clay is a silty clay which is used in some countries, notably Spain and South America, for the erection of walls of dried mud. It is seldom used in Great Britain to-day, but was formerly much used for "cob cottages."

Alluvial clay is used for brickmaking in localities where no more suitable clay is obtainable; its irregular composition prevents it from being of great value.

Alum shales are indurated clays from which alum is obtained. The sulphides in the clay are oxidised by exposure to the air or roasting, and the sulphates produced are washed out, the solution being evaporated until the crystallisation stage is reached.

Any clay or shale sufficiently rich in pyrites or other readily oxidisable sulphide may be used for the production of alum. (See the **Alum Industry**, p. 55.)

Ball clays are relatively pure white-burning clays which are characterised by their great plasticity. The term is used to include clays differing greatly in quality and composition, many ball clays burning to a light brown colour instead of white. British ball clays are characterised by the relatively low temperature at which vitrification (p. 153) occurs, though the mass does not begin to lose its shape until a temperature beyond the usual working limits of the kilns used by potters is reached. This property, combined with the high degree of plasticity, makes ball clays extremely valuable for the manufacture of earthenware and stoneware (*q.v.*).

By the judicious use of white-burning non-plastic ingredients and of minute quantities of cobalt oxide, the potter is able to neutralise the colour of the burned ball clay and to produce a ware of sufficient whiteness. For stoneware, the vitrification which occurs on heating ball clays produces a mass of great strength and imperviousness to liquids; the colour of the product is regarded as of minor importance. The most valuable deposits of ball clay in the British Isles are in Dorset and Devonshire.

Boulder clay is a term used by geologists to distinguish the clays deposited by glacial action. Broadly speaking, the boulder clay extends over the whole of northern England and over much of the Midlands and Ireland, but much of it is quite useless owing to the stones and sand deposited with it. The cleaner portions of the boulder clay are used for the manufacture of bricks and roofing tiles, and in a few isolated cases coarse glazed pottery is made from it.

The stones and gravel which are a characteristic feature of this clay may be removed by washing or screening, or they may be crushed to powder; the former method is the more effective but the latter is cheaper and for common bricks gives a useful product, provided that limestone is not present in large proportion.

The limestone becomes converted into lime in the kiln, and when the bricks are exposed to the air, the lime hydrates and expands, cracking the bricks or breaking them to pieces. The only remedy consists in either removing the limestone, as indicated, or in grinding it so fine and heating the bricks to such a temperature that the lime enters into combination with the clay, forming a glassy compound which does not expand appreciably on exposure.

Brick clays and **brick earths** are those specially suitable for the manufacture of bricks, though the latter term is usually confined to superficial clays which are suitable for hand-made bricks and is specially used in connection with certain clays in the London Basin, Kent and Essex, such bricks being known as **London Stocks** or **Kent Stocks.**

For brickmaking, a clay or earth must contain sufficient sand to reduce the shrinkage in drying and burning to within reasonable limits (usually about 1 in. per linear foot), as otherwise the clay will crack or twist unduly. To mix sand with a highly plastic clay necessitates the use of powerful machinery or the expenditure of much time and labour, so that those clays pre-eminently suited for brickmaking are the ones which naturally contain sufficient sand, and would be more correctly termed **loams** than clays.

The chief characteristics required in a brick earth are moderate shrinkage, great strength when burned, and good colour when taken out of the kiln. If these requirements are satisfied, the composition and other properties may be regarded as of secondary importance.

Cement clays are those specially suitable for the manufacture of Portland cement and similar substances (see p. 85). They must be very siliceous, but free from more than a very small percentage of magnesia. High class shales are generally used for the purpose, as plasticity is of no importance, and is, in fact, an objectionable property.

The cement works on the Thames and Medway use alluvial mud which is mixed with chalk, but in Cambridgeshire a naturally occurring mixture of clay and chalk (**Marl**) is preferred.

China clay is a white burning clay of low plasticity which is usually found close to the place of its original formation by the decomposition of igneous rocks. The only deposits of importance in Great Britain are in Cornwall, though small quantities are found in other localities. The term **kaolin**[1] refers to any clays having the general characteristics of china clay, quite independently of their origin, so that unless care is taken, confusion may easily arise. When separated from the coarser rock particles, by washing, china clay and the purer kaolins contain about 90 per cent. of true clay and, so far as composition is concerned, a carefully selected and refined china clay approaches more nearly to a pure clay than any other clay known. Such a clay is exceedingly resistant to heat (corresponding to Seger cone 34 which has a softening point of 1,750° C.) but its low plasticity prevents it being used for many purposes for which the somewhat less pure, but highly plastic, ball clays and fire-clays are eminently useful.

China clays and kaolins are used in the manufacture of porcelain (p. 195) and owe their name to the fact that they are the chief clay used in the manufacture of china ware (p. 187). Still larger quantities are used in the manufacture of paper, and the very finest qualities are used for the manufacture of ultramarine. In the manufacture of earthenware, china clay gives an added whiteness to the body, whilst being more plastic than flint—the other agent used for the same purpose.

Crucible clays are selected fire-clays, mixed with burned fire-clay or grog and sometimes with 3–30 per cent. of plumbago or blacklead to increase their resistance to sudden changes in temperature, and to secure more complete reducing conditions when melting metals and reducing ores. The quality of a crucible depends very largely on the mixture employed having the requisite characteristics, and it is seldom that good crucibles of large size can be made from a single clay.

---

[1] See also Sections LXV., LXVI., and LXVII.

It is customary to use several clays of similar origin, but of slightly different properties, the low cost of a local fire-clay (where such is obtainable) causing it to be used in some instances even when better crucibles could be made by substituting a slightly more expensive clay. The mixtures used vary with the purposes for which the crucibles are to be employed, and the temperatures to which they are to be heated. It is therefore useless giving special recipes here, as each crucible manufacturer has to adapt his mixtures to the needs of his various customers.

Fire-clays are those which have a notable resistance to the action of heat. It is not customary to include clays under this term unless they are at least as resistant as Seger cone 26 (1,580° C.).

The fire-clays occur chiefly in the coal-fields and in close association with coal, the most famous being those near Stourbridge, around Leeds and in Yorkshire generally, and the fire-clays in West Scotland, of which Glenboig is commonly regarded as typical. For export purposes the fire-clays in the Northumbrian and Durham coal-fields are particularly well known. Other deposits of fire-clay occur in other localities and have a local reputation, especially in Derbyshire and Wales.

Apart from resistance to heat, the most important characteristic of fire-clays is the production of goods of small shrinkage with sufficient resistance to abrasion and corrosion and of accurate shape.

Fuller's earth is a term applied to any earthy matter which will act as a grease absorbent, but true fuller's earth is not unlike a china clay, though it differs from the latter in several respects, notably in composition, being more allied to a marl.

Careful analyses suggest that fuller's earth is largely composed of montmorillonite, but does not correspond exactly to it. The most important deposits occur in Surrey, Kent, and Bedfordshire. At the present time, large quantities of china clay are sold as fuller's earth, especially for toilet purposes.

Ganister is a rocky mineral with a composition corresponding to a pure silica mixed with a very small proportion of clay. It is used in the manufacture of siliceous fire-bricks (p. 223) and for lining furnaces. It is not a true clay though the term **Ganister clay** is often used. Ganister is part of the "Farewell Rock" of the coal measures.

Grog is a burned clay which is added to raw clay to reduce the shrinkage of the latter. In refractory wares it also serves as a skeleton which preserves the general shape of the articles in the kiln. Its properties vary with the clay from which it has been made by simple calcination.

Kaolinite is one of the most characteristic of the clay-minerals (p. 150) and is the chief constituent of some of the purest clays (kaolins) yet isolated, viz., $H_4Al_2Si_2O_9$.

It has, for this reason, been regarded as the essential constituent of all clays, but this is incorrect. Its lack of plasticity may be due to its compact crystalline form.

Loams are natural mixtures of clay and sand, and are useful for the manufacture of bricks, tiles, and similar articles. They play an important part in agriculture.

Marls are natural mixtures of clay and chalk, and are specially suitable for the manufacture of cements and for certain kinds of bricks.

Many of the stock bricks used in Essex are made of artificial marls or **malms**, prepared by mixing chalk and clay together with water in a wash mill. The term marl is also applied to brick-earths which are devoid of chalk, as in Staffordshire, where the so-called marls used for the famous blue engineering bricks are clays occurring in the Upper Coal Measures.

Pipeclay is primarily any clay suitable for the manufacture of clay tobacco pipes, but it is now applied to all whitish clays.

It occurs in small quantities in many localities, but the chief deposits are in Devonshire and North Derbyshire.

Puddling clay is any plastic clay which will form a waterproof backing or lining to a reservoir or similar structure; they must dry without cracking.

Red-burning clays are those which are red in colour after being heated to 800° C. or above. They are chiefly used in the manufacture of bricks, tiles and terra-cotta. The colour is due to iron compounds, the precise nature of which has not been satisfactorily explained. The composition varies within wide limits, and even the percentage of iron present appears to bear no simple ratio to the intensity of the colour produced.

The best red-burning clays are the Midland marls, the Welsh clays typified by Ruabon, and the Lancashire clays typified by Accrington, but such excellent red-burning clays can be found in other parts of the country that it is probably more correct to say that the localities mentioned owe their reputation rather to the size of the works and the skill of the men engaged in them than to any very exceptional quality in the clays themselves.

In the production of terra-cotta, bricks and tiles from red-burning clays, the chief requisites are uniformity of colour, quality of colour, strength or resistance to crushing, and accuracy of shape. **Slowness of heating**, combined with an ample supply of air, is the chief means of obtaining a good red colour; if the temperature rises too rapidly, and there is a lack of air, the iron compounds in the clay become reduced to the ferrous state and then rapidly combine with the clay, forming vitrified and slag-like compounds of a dark blue, grey or black appearance. Usually these darker tones are more abundant near the centre of the bricks, and are then known as **hearts** or **cores**; if very extensive, the gases produced in connection with these cores will cause the bricks to swell, and will give them a partially molten appearance, rendering them almost useless for structural work. If the heating is effected very slowly, and sufficient air enters the pores of the bricks or other articles, the iron compounds will remain oxidised, even when any carbonaceous matter in the clay is being burnt out, and the bricks will retain their true shape, and will have the desired colour. As slow heating is expensive, the tendency of all brickmakers is to hurry the burning but in proportion as they do so with close textured clays, so do they increase the risk of dark coloured and swollen goods. If the plasticity of the clay is sufficiently great for sand to be mixed with it, this will open the pores and so shorten the time required for the heat and air to penetrate the bricks. The proportion of sand which can be added is, however, limited, as it depends on the binding power of the clay. An excess of sand will make the bricks so soft that they can be rubbed to pieces by rubbing them against one another. For the erection of specially shaped arches, such soft bricks are made on purpose, and are termed **rubbers**.

Many attempts have been made to improve the colour of red-burning clays by the addition of red oxide of iron; such attempts usually end in failure, as the colouring matter must be in a far finer state of division than commercial iron oxide, and it must be distributed throughout the clay in a far more uniform manner than is possible with an ordinary mixer. The addition of ochreous clays is more satisfactory, but is too costly, and the only means of making a poor-looking clay into a good red brick is to apply a dip or cream, composed of good clay and water, to the defective brick before it enters the kiln. If the composition of the dip is correctly adjusted, the bricks will then have a good red exterior; inside they will, of course, be as unpleasant as before, but this will not matter so long as the bricks are not chipped or broken.

Refractory clays have been described under **Fire-clays** (p. 156), but china clay is also a refractory clay.

Sagger clays are fire-clays specially suitable for making cases or saggers in which pottery is placed when in the kiln or oven.

The requirements of a sagger clay are similar to those of a crucible, but as the saggers are usually much larger and shallower, it is even more important that they should not lose their shape when heated. The best saggers are made of a mixture of fire clay and grog.

Shales are indurated clays which have lost their original texture, and have become hardened into a stony mass, the chief characteristic of which is the curious laminations of which it is composed.

Many shales are so siliceous as to be almost devoid of clay, but the clay shales as a whole are excellent brickmaking materials. They require to be ground to powder before use; the grinding restores them to something like their original condition, so that when the ground shale is mixed with water it becomes plastic. Some shales are almost as refractory as fire clays, but the majority of British clay shales produce ordinary red or buff bricks.

Oil shales contain a sufficient proportion of bituminous matter to permit oil to be distilled from them in commercially profitable quantities (see **Martin's** "Industrial Chemistry: Organic"). Some of the richer shales produce no less than 40 galls. of crude oil per ton of shale.

Alum shales have already been described (p. 154).

Slates are hard clayey rocks, often very dark in colour on account of the carbonaceous matter present, and may be regarded as shales which have been subjected to heating and pressure.

They are extensively used as a roofing material, and the refuse from the slate quarries is occasionally ground and used for the manufacture of bricks. Its hardness and lack of plasticity are, however, against its use for this purpose in most localities, and it may be regarded as of little value.

The chief British slates occur in the Lake District, Wales, Cornwall, and in various parts of West Scotland and Ireland.

Soils are essentially mixtures of clay and sand, but calcareous soils or marls (p. 156) are also of importance in agriculture.

The composition of soils varies very greatly, and in spite of the vast amount of research carried out on the subject, there is still but little known as to what really constitute the desirable qualities of soils for many crops. The productiveness of a soil appears to depend on its porosity or means of introducing air and water to the roots of the plant, and on the proportion of soluble salts contained in it in a form in which they are useful to the crops. As these soluble salts are removed the soil becomes impoverished, and its food-content must be renewed by the addition of fertilisers and manures. The decay of vegetable and animal matter in the soil induces acidity which must be neutralised by the addition of lime, but the subject of lime fertilisers is too complex to be dealt with here. Most virgin soils are too heavy to be used without some preparation, and must therefore be broken up mechanically. Many soils must also be made more porous by the addition of non-plastic matter such as chalk, sand or lightly burned clay. For further information on soils, the reader should consult some of the many excellent text-books on the subject of agriculture.

Surface clays are those which occur on the surface of the ground or immediately below the soil.

They vary enormously in character according to their origin and mode of deposition, and in some localities are weak and sandy, whilst in others they are strong, tough, and highly plastic. The latter are useless for manufacturing purposes unless a suitable sand is available, and a mixture of sand and clay can be made at a sufficiently low cost.

Tender clays are usually highly plastic, and consequently they cannot be used for the manufacture of bricks or pottery without the addition of some non-plastic material.

They are termed "tender" because when ordinary methods of manufacture are used, these clays crack or twist, or otherwise cause trouble on account of their apparent inability to withstand the ordinary treatment. This tenderness may usually be overcome by the addition of a suitable material, but the effect of this addition is, usually, to change the properties of the clay to such an extent as to make it unsuitable for the purposes for which it was proposed to use it. Thus, many tender clays burn to a delightful colour, but the addition of sand converts them into very "ordinary" bricks, and the specially attractive colour is lost. Where such special characteristics are to be retained, the services of an expert in clay working must be requisitioned, for the recent advances in this direction are beyond the powers of the average brick maker, building manufacturer or kiln builder. With the right treatment, it is now possible to retain almost all the good qualities of tender clays and to overcome their tenderness.

Vitrifiable clays are those which are impervious to water after they have been burned in a kiln or oven. This imperviousness is valuable in itself as enabling articles of such clays to be used for containing liquids of various kinds, without the necessity of using glazed ware, but the vitrifiable clays are chiefly valued on account of the strength of the ware made from them. If a pure clay is heated it remains porous until a temperature beyond the reach of commercial kilns is reached, when it gradually melts and loses its shape. With a vitrifiable clay, on the contrary, there is a sufficient proportion of fluxing material present for some of the constituents of the clay to commence to fuse at a dull red heat. As the temperature rises more and more fused matter is produced, and this gradually fills the pores in the clayey mass. Finally, a stage is reached when all the pores are filled, and if the heating is continued still further the mass will lose its shape. In some cases the corrosive action of the fused constituents is so great that the mass loses its shape even before all the pores are filled; such clays are less valuable for commercial purposes.

The best vitrifiable clays (so far as British clays are concerned) are the ball clays occurring in Dorset and Devonshire, but artificial mixtures are frequently made by the judicious use of fire-clay and felspar or some other suitable flux. Lime compounds are undesirable for this purpose, as they are too violent in reaction, and bring about a premature loss of shape. Magnesia compounds, on the contrary, give a long range of vitrification, and produce impermeable wares at a temperature considerably below that at which loss of shape occurs.

The vitrified mass produced when vitrifiable clays are burned at a suitable temperature consists essentially of a skeleton of refractory clay, the particles of which are bound together by a glassy magma formed of the fused constituents. Bricks and other articles made of clay must usually contain some vitrified matter, as without it they would be so weak as to be useless, but the term "vitrified" is usually restricted to those articles which do not absorb more than 1 per cent. of water on immersion for twenty-four hours. The enormous resistance to crushing which is so characteristic of blue bricks is due to the large proportion of vitrified material in them, this material being increased by the reducing conditions under which such bricks are burned. As previously explained, the ferric compounds in a brick heated under oxidising conditions only act as colouring agents, but in a reducing atmosphere the ferrous compounds form a vitrified mass with a long range of vitrification, and yield a material which is fully as valuable as magnesia for this purpose.

Yellow or Buff-Burning Clays are usually fire-clays, but some vitrifiable clays in the Midlands produce yellow bricks, and some mixtures of red-burning clay and chalk used for *stocks* in various parts of the South of England produce bricks which are of a pale primrose tint.

Ordinarily a clay which has more than 3 per cent. of iron (expressed as ferric oxide) will produce red or terra-cotta ware when burned, but if a sufficient proportion of calcium carbonate is present or is added in the form of chalk, this will combine with the iron and clay and will form a white brick, a yellow tinge being produced if the lime has not combined with all the iron. Clays with less than 3 per cent. of iron as ferric oxide will, if sufficient true clay be present, burn to a buff or primrose colour, but if much fluxing material is present a dark-coloured brick may be produced.

ANALYSIS OF CLAYS

From what has been stated on previous pages, it will be understood that the published analyses of clays are of minor value, inasmuch as most of them are very incomplete. To omit an actual determination of the "alkalis" (potash and soda compounds) and to fill in the blank thus caused by deducting the sum of the other constituents determined, is almost unpardonable, for a difference of only ¼ per cent. in the amount of alkalis present will make all the difference when a selection is to be made between two clays of similar composition, or where a clay of exceptionally high resistance to heat is needed. In most published analyses all that is shown is the relative proportions of alumina and silica with those of such oxides as iron, lime, and magnesia. For non-refractory clays this information tells little or nothing of value; for refractory clays it is almost useless unless an accurate statement of the percentage of potash and soda is also present. There is little information to be derived from an analysis which cannot be known equally well by determining the fusing point of the clay (relative to Seger cones), and from the appearance of the raw and fired samples, and analysis is only of value in comparing clays where the composition must be known with considerable accuracy in order to make the necessary adjustment of the mixtures used in porcelain or earthenware bodies. For most purposes for which analyses of clays are made, however, it would be better first to examine the clay in the manner indicated above and to leave the analysis to a later stage in the investigation. By this means many unsuitable clays can be sorted out at a small cost, whereas an analysis, if it is to be of any value, is a tedious and costly piece of work. Some of the precautions required are stated in J. W. Mellor's "Quantitative Inorganic Analysis" (London, 1913).

In various text books a method is described which purports to shew how clay may be separated from the other constituents of a mixture. This consists in treating the clay with hot sulphuric acid, which is supposed to dissolve the clay and to leave felspar, mica, and other associated minerals (sand) unattacked. Segar devoted much attention to this process, and with a limited number of kaolins it yielded useful but often very erroneous results.

There is, at the present time, no really definite means of ascertaining accurately the proportion of "true clay" in a sample, and the best that can be done is to eliminate other coarser particles by careful washing or elutriation, and then to make an analysis and microscopical examination of the finest particles. As few other substances are so finely divided as clay, this method gives results which are more accurate than would generally be supposed.

What is known as a "differential thermal analysis" is obtained by heating a clay and an inert substance (such as highly calcined alumina) separately at a steadily rising temperature and plotting the differences in the temperature between them throughout the heating on a time-temperature graph. Such thermographs often give valuable information of the proportions of various constituents of the clay (see Butterworth's book (pp. 135–8) mentioned on p. 213).

An analysis of a clay may be expressed in terms better understood by the average man by recalculating the "ultimate analysis" of the finest particles into clay, felspar or mica, and free silica, on the basis that all the lime, magnesia, and alkalis are in the form of felspar or mica, the remainder of the alumina and a proportionate quantity of silica are in the form of kaolinite or other clay of the same composition; any silica then left over being regarded as present in the free state. This calculation, which is purely empirical, and is open to numerous objections, is, at present, the nearest approach to a proximate analysis of clay which has yet been devised. If taken in conjunction with a microscopical and petrological examination of the clay it will give results which are at least intelligible to the clay worker, even though not of the highest scientific value. The serious error in such a method lies in the assumption that the true clay actually present is of the same composition as kaolinite; in reality many of the clay minerals (especially those in fire-clays) appear to be richer in silica. The error caused by understating the clay and overstating the free silica does not, however, prove serious in practice. In some cases the assumption that the oxides are present as mica or felspar is more serious, but with the present state of knowledge it is difficult to avoid this error.

Physical tests of clay are of considerable importance, but are too numerous, and require too lengthy a description to be included here. Readers interested in them will find detailed descriptions in "The Clayworker's Handbook," in "British Clays, Shales, and Sands," and in "The Chemistry and Physics of Clays" (see Literature, p. 149).

PHYSICAL TESTS

For most industrial purposes the physical properties are much more important than chemical analyses. The changes—when clays are heated at various temperatures—in volume-weight, specific gravity of the individual particles, porosity, refractive index, various optical properties, coefficient of expansion or contraction, resistance to constant pressure (particularly as showing the refractoriness-under-load), and, in some cases, resistance to acids, alkalis, slags, or molten metals are of great importance in ascertaining the usefulness of clays and of articles made from them.

The great amount of attention paid to these changes during the last fifty years has effected what may be called a revolution in our knowledge of clays, and of their behaviour and the uses which can be made of them.

SECTION LXV

POTTERY

By Alfred B. Searle

Revised by Marcus Francis

LITERATURE

A very complete Bibliography of Pottery prior to 1910 is contained in—

A. B. Searle.—"The Clay-Worker's Handbook." London, 1911.
M. Solon.—"Ceramic Literature." London, 1910.

Among the many recent works (excluding books solely for collectors of pottery) the following may be mentioned:—

A. B. Searle.—"An Encyclopædia of the Ceramic Industries." Ernest Benn Ltd., London, 1930.
Dept. of Commerce.—"The Pottery Industry." Govt. Printing Office, Washington, 1915.
"Ceramic Products Cyclopedia." Industrial Publications Inc., Chicago, 1932.
"Directory of Ceramic Materials." Ceramic Industry, Chicago, 1942.
E. Rosenthal.—"Porcelain and other Ceramic Insulating Materials." Chapman & Hall, London, 1944.
—— "Pottery and Ceramics." Pelican Books, 1949.
Ed. P. McNamara.—"Ceramics, Clay Products, and Whitewares." Penn. State College, 1938–44.
R. Newcomb.—"Ceramic Whitewears." Pitmann, New York, 1947.
J. B. Kenny.—"The Complete Book of Pottery Making." Greenberg, New York, 1949.
F. Singer.—"Ceramic Glazes." Borax Consolidated Ltd. London, 1951.
—— "Die Keramik." G. Springer, Berlin, 1923.
W. Funk.—"Rohstoffe der Feinkeramik." G. Springer, Berlin, 1933.
H. Hecht.—"Lehrbuch der Keramik." 1930.
W. Pukall.—"Grundzüge der Keramik." Sprechsaal Verlag, Coburg, 1922.
H. Salmang.—"Die Keramik physikalischen und chemischen Grundlagen." G. Springer, Berlin, 1951.
D. Arnaud et G. Franche.—"Manuel de Céramique industrielle." Soc. Fr. d'Ed. Litt. et Tech., Paris, 1934.
F. Greber.—"Traité de Céramique." (Encycl. Roret.) Dunod. ed. Paris, 1922.
A. Granger.—"La céramique industrielle." Paris, 1929.
F. H. Norton.—"Elements of Ceramics." Cambridge, Mass., 1952.

Original papers dealing with the technical and scientific side of pottery will be found in the official publications of the British, American, and German Ceramic Societies, but articles of technical interest appear from time to time in the various trade journals devoted to the pottery and glass industries. The Ohio State University Experimental Station publishes bulletins of ceramic interest from time to time. The German pottery industry has been dealt with in a number of B.I.O.S. reports, some of which go into considerable detail regarding technical processes and batch recipes.

Pottery has always held an important place among the essential requirements of life, and its use has now extended to such an extent that it is difficult to realise the dependence of the industrial world upon it.

Without pottery there could not be the convenient employment of electricity we now enjoy; the production of the highest grades of steel and of most other products of the furnace would be impossible; there would be no bricks or tiles; the production of corrosive chemicals, with all that depends thereon, would be reduced to an insignificant quantity; the use of crucibles for testing and for refining purposes would remain unknown. In short, a modern industrial state without many diverse forms of pottery is almost inconceivable.

There is, in fact, as Brongniart has remarked, "no industry that affords in its practice, in its theory, or in its history, so many interesting considerations in the wealth of its scientific and economic application as the ceramic art or the manufacture of vessels and utensils out of baked earth. Nor do I know one that offers productions more simple, more varied, more easy to make, or more durable in spite of their fragile construction. In no other human product are so many qualities united."

The Classification of Pottery.—The term "pottery," like several others which are equally familiar, is almost incapable of exact definition. It is generally understood to include all articles made of earthy materials, as in the use of the word "earthenware," but so broad a definition gives but little idea of the nature of pottery. As soon as a more precise definition is attempted, however, difficulties arise which are so serious as to render such attempts at a general definition quite unsatisfactory.

It is frequently stated that "pottery" is definable as "articles made of clay," but in view of there being no really satisfactory definition of clay, and the existence of a large amount of pottery in which clay is by no means the largest constituent, this statement becomes unreliable.

A similar difficulty is experienced when it is desired to classify the various kinds of pottery, and no entirely satisfactory classification has yet been devised.

In many respects a modification of Knapp's classification is adequate; it may be summarised as follows:—

1. *Porous Pottery.*
(*a*) Unglazed pottery.
(*b*) Terra-cotta, bricks, tiles and refractory ware.

2. *Non-Porous Pottery.*
(*c*) Earthenware.
(*d*) China and porcelain.
(*e*) Stoneware.

There are several anomalies in this, as in all other classifications of pottery; *e.g.*, the porosity may be understood as relating to the general substance or *body* of the article, quite apart from the use or absence of a glaze. Thus, earthenware which is glazed is, to all intents and purposes, non-porous, though apart from the glaze it is highly porous.

(*a*) *Unglazed pottery* consists of a plastic, earthy material which has been made into the required shape, and then heated in a kiln or oven until it has been converted into a stone-like mass of medium hardness and great durability. Strictly speaking, the term "unglazed pottery" includes the articles mentioned in group (*b*), but it is more convenient to confine it to hollow-ware articles.

(*b*) The *terra-cotta*,[1] etc., group includes all solid articles, made of earthy materials, which are of a porous nature. The members of this group are usually soft enough to be scratched by iron, but some of them are so hard, or have a superficial hardness so great, that they cannot be scratched by steel.

The pottery in the two foregoing groups consists typically of burned clay, its colour varying from light yellow to red, reddish brown, and finally to a colour so dark as almost to approach black. If the raw materials used are exceptionally pure or are rich in lime, the pottery may be quite white.

If the temperature to which the pottery is heated in the kiln or oven is sufficiently high, the material of which the goods are made will begin to fuse and to lose its porosity and shape. With most clays this occurs at a temperature of about 1,000°-1,350° C., but if a pottery material can withstand the action of a kiln at a temperature of 1,500° C., or above, it is usually placed in a separate class as a heat-resisting or refractory material. Such refractory ware is usually soft enough to be scratched by iron, though parts of the surface may be harder, especially if the temperature of the kiln has been very high.

When a piece of porous ware has been heated to such a temperature that the fused matter formed commences to fill the pores, the article will generally begin to lose its shape and to become twisted or warped. If it does not do this, it should be classified among the non-porous pottery. Thus, a brick clay will ordinarily be used for porous ware such as bricks and tiles, but by heating it in a kiln to a higher temperature than usual, a crude kind of (non-porous) stoneware may be obtained. Reducing conditions at certain stages of the firing favour this.

(*c*) *Earthenware* consists of porous pottery covered with a coating of glaze. It is, therefore, impermeable so long as the glaze remains sound and whole, but any damage to the glaze will simultaneously increase the porosity. The appearance of articles made from natural clays may often be improved by interposing a white burning clay between body and glaze, giving the effect of articles wholly of the more expensive clay. In some instances an opaque glaze or enamel serves the same purpose by covering any defects of colour or texture in the clay of which the earthenware is made (see also Section LXVI.).

---

[1] *Terra*, earth; *cotta*, baked. The term is used in the arts with reference to a particular colour, but in pottery its original significance of baked earth is retained, and is quite independent of the colour of the ware (see Sections LXIX. and LXX.).

The term "earthenware" is very elastic, and comprises pottery of widely different values, including the crude efforts of peasants in semicivilised countries, as well as the most elaborate work of the most gifted earthenware manufacturers in the world—work for which the British potters have been famous for many years, and for which they continue to maintain their reputation.

On the Continent, the term *faience* is used for all glazed articles other than stoneware and porcelain, and is therefore applied to earthenware. The term *majolica* is used to indicate a faience or earthenware in which the body is covered with an opaque glaze or enamel; this term is used somewhat loosely, and is occasionally, but erroneously, applied to ware covered with an opaque body over which is a transparent glaze.

Chinaware and porcelain are the most valuable forms of pottery so far as beauty of form, texture, and decoration are concerned. It is, indeed, a cause for perpetual wonder as to how it has been possible for such lovely objects to be manufactured (see Section LXVII.).

The term "porcelain" is applied by collectors and others to so many kinds of pottery that it cannot be defined at all accurately, though all true porcelains possess certain clearly recognised characteristics. Amongst these are the imperviousness of the body, the fineness of finish, and the whiteness of the undecorated portions of both the body and the glaze, the general hardness of the ware, and the translucency of the thinner portions of it. But the chief characteristic which distinguishes the porcelains from all other kinds of pottery is the manner in which the light is reflected from their surface. Some of the best specimens of earthenware and stoneware attain a translucency and hardness quite equal to that of porcelain, yet they cannot compare with the subtle and beautiful effect produced by the play of light on porcelain because of the difference in the texture and surface of the latter. This is due to the glaze in a true porcelain having a composition and nature very similar to that of the body to which it is applied, so that the transition from the outer surface of the glaze to the body of the ware is delicately gradual instead of being abrupt as in other forms of pottery. When the light falls on the surface of a piece of true porcelain it is reflected back by myriads of tiny crystals, each surrounded by a glassy substance, so that it emerges, softened and subdued, in a manner which is exquisitely beautiful, and is quite impossible of attainment in any other kind of ware.

There are many kinds of porcelain—indeed each different works must perforce produce a porcelain differing slightly, yet recognisably, from the others, and a perfect imitation is almost as impossible as it would be undesirable. Hence, the products of all the well-known firms may readily be identified by the expert without any reference to makers' marks. Yet, notwithstanding the multiplicity of the porcelains, they may be classified in three main groups according to their composition, viz.:—

(*a*) *The natural or true porcelains* consisting essentially of a mixture of clay and felspathic material with a glaze of similar composition, but more fusible; represented by the Chinese and Japanese porcelains as well as by the "hard paste" porcelains of Continental Europe.

(*b*) *The artificial or glassy porcelains* which were made from a mixture of clay and fused silicate or frit in the eighteenth century in various parts of Europe.

These porcelains are known as "soft" or "tender" and were difficult to produce because of the low plasticity of the raw materials and the liability of the articles to warp or lose their shape when in the oven.

(*c*) *Chinaware or bone porcelains*, invented in England, which is still the main manufacturing country for this ware. These consist of a mixture of clay with calcined bones and a naturally occurring mixture of felspar and quartz known as china stone.

The product is intermediate in properties between the other two groups of porcelain, though bearing a closer resemblance to the natural porcelains than to the artificial ones.

These three groups of porcelain may also be sold in an unglazed state, forming a number of wares of which *Parian* or *statuary porcelain* is the best known.

Both the tender porcelains and the chinaware are incapable of the beauty of the finest specimens of hard porcelains because, in the former, the glaze used is fired at a temperature much below that required for the ware itself, whereas in the true porcelains the glaze and the body are both finished at the same temperature and a far more homogeneous product is obtained.

The manufacture of true porcelain has rarely proved commercially profitable in Great Britain, and by far the greater part of English porcelain is of the bone porcelain or chinaware type. The British Government, in the 1914–18 war, voted a sum of money to be spent in endeavours to produce a good, hard porcelain from British materials.

For further details, see Section LXVII.

Stoneware consists of a non porous body which may, or may not, be covered with a glaze. It is distinguished from porcelain by its lack of translucency, by its colour and by its coarse nature, and from earthenware and terra-cotta by its imperviousness to water. This impermeability is never absolute, and most unglazed stoneware will absorb a fraction of one per cent. of water; hence there is no sharp dividing line between stoneware and terra-cotta, though in practice little confusion arises in classifying these wares.

The term "stoneware" is frequently applied to coarse glazed ware used in sanitation (such as kitchen sinks and drain-pipes), although such ware has a porous body which has been made externally impervious by a coating of glaze usually formed in the kiln by putting salt on the hot fire. Some of the finest stoneware has some resemblance to the cruder porcelains, but is readily distinguishable by its different texture and action on light.

For further details, see Section LXVIII.

The **physical properties of pottery** differ according to the nature of the ware and cannot well be considered in general terms.

For domestic and sanitary purposes, pottery must be convenient in shape, entirely impervious to water, milk and the various fluids used in cookery, and sufficiently strong to withstand ordinary wear and tear and such sudden changes in temperature as are ordinarily experienced in its use. It should also be pleasant in appearance and capable of such decoration—both in carved work and in colouring—as will increase the pleasure felt in using or in seeing it.

For *technical purposes*, pottery must be capable of withstanding ordinary usage, and must be sufficiently resistant to the fluids to which it will be subjected. The glaze (if any) must be tough enough to last for a reasonable time, and the ware as a whole must be strong enough to carry any loads or to resist any electrical current to which it is likely to be subjected. In some branches of manufacture, pottery must be capable of being repeatedly heated and cooled without any cracks forming in the glaze or body and, in the case of drain-pipes, it must be sufficiently tough to permit a small amount of ground settlement without fracture.

For *architectural work*, a number of other characteristics are required. Building bricks and terra-cotta must be sufficiently strong to carry the loads imposed on them; the more refractory bricks and slabs used in the fireplaces and chimneys must be capable of resisting any probable temperature, whilst flooring tiles and paving bricks must be intensely hard and tough so as to withstand the wear and tear of traffic over them. In addition to strength, most architectural pottery (including bricks and tiles) must have a pleasing appearance, especially that which will be seen when the building is completed. For interior brickwork, the colour and appearance are of minor importance, but for exterior work they are first qualities sought by the architect, although strength and resistance to crushing are equally important in large structures.

For *purely decorative purposes*, the clearness and quality of the colours, brightness of the glaze (if any), and the texture of the visible surfaces of the ware are of the greatest importance, and it not infrequently happens that physical defects which result in an attractive appearance are not merely tolerated but are actively welcomed. The cracked glaze in "crackle ware," and the irregular flow of coloured glaze on tiles and vases, are two typical examples of defects of this character which are used for the purposes of ornamentation and decoration.

In many pieces of decorative pottery, properties of importance for other purposes are deliberately neglected in order to obtain beautiful effects not otherwise procurable. Thus, an article for indoor use need not possess the durability and resistance necessary in ware intended to be exposed to the weather and it is, therefore, possible to use colours and to obtain effects which are quite impossible when weather-resisting pottery is required.

The decorative value of pottery depends almost entirely on the technical skill and on the æsthetic feeling possessed by those engaged in its manufacture. Its beauty is not confined to colour, design or form, for pottery offers greater possibilities to the artist and sculptor than does any other material. Each year the number of available colours increases, each year an increased mechanical exactitude in manufacture is obtained. It is still true that pottery is one of the most conservative as well as one of the most progressive arts, yet the progress made in manufacture during the last half century is remarkably great. The modern potter with more precise technical and scientific knowledge of the materials used, and better methods of heating them than was possessed by his predecessors, is continually finding new materials and new effects with simpler and more reliable methods of manipulation. At the same time, the increasing demands of other departments of industry are opening out fresh fields of service to the manufacturer of pottery, and are increasing the value of this material both industrially and æsthetically.

For most practical purposes the cross-breaking strength (Modulus of rupture) may be taken as an indication of the "strength" of a pottery body. It can be measured with comparatively simple equipment with an accuracy well within the uncontrollable differences between the measurements on different test specimens. The compressive strength is generally some 6 to 10 times greater, and the tensile stress less by a factor of about 3 or 4. Impact strength is very much lower than even tensile strength; this is, perhaps, the greatest drawback to pottery bodies as engineering materials: it is due to the low elasticity of ceramic materials.

For one and the same type of body the maximum strength is not developed until the porosity (which depends on the "hardness" of firing) has been reduced to a minimum: hence a vitreous body is nearly always mechanically stronger than a semi-vitreous or slightly porous body of the same general type, though it may be less resistant to impact. The strength also depends on the method of making: thus test pieces made from plastic clay are generally stronger than those from dust-pressed clay of the same composition. De-airing usually results in a perceptible increase in strength, while glazing may result in a marked increase in strength, provided the glaze is properly adjusted to the body. To go into these matters in more detail is outside the scope of this work.

As the static strength of pottery bodies is usually more than sufficient, a body which is not quite vitreous may stand up better to the rough and tumble of domestic or hotel use, in virtue of higher impact strength, than one which is completely vitrified.

Table I., containing information culled from various sources, is intended to be nothing more than a general guide to the figures likely to be obtained for the type of pottery ware indicated. More detailed information may be obtained from books of tables, such as the International Tables, or from original sources.

TABLE I.

ORDER OF STRENGTH OF POTTERY BODIES.

(Approximate only as there is considerable overlapping, particularly in the medium and low strength regions.)

Cross-breaking strength in 1,000 lbs. per sq. in.				
20	Special bodies: clino-enstatite, zircon porcelain, titanium bodies, etc. (see electrical porcelain)			
	Steatite porcelains	Fully vitrified, non-porous bodies	Highest impact strength	Hard-fired
	Hard-paste porcelain			
15				
	High-tension electrical porcelains			
	Dense, chemical stoneware			
	Bone china	Incompletely vitrified, low-porosity bodies	Intermediate impact strength	Medium-fired
10	Low-fire vitreous bodies			
	Fine stoneware			
	Hard-fired earthenware			
	Common stoneware			
	Low-tension electrical porcelains			
	Porous earthenware	Porous bodies	Low impact strength	Easy-fired
5	Common stoneware			
	Fire-clay bodies			
	Dust-pressed tile bodies			
	Red clay, terra-cotta, etc.			
	Marl and other porous clay bodies			
0	"green," *i.e.* unfired bodies			

The manufacture of pottery has undergone many changes during the last few decades, and the modern custom in America and Europe of building very large factories and working them in the most up-to-date and progressive manner possible is making it increasingly difficult for the smaller firms both in this country and abroad. The rapid increase in American potteries is also tending to close one of the best markets open to British potters. In the newer countries, competition amongst British, French, and German potters is very keen, and the progressiveness of French and German potters has made their influence felt on the home trade of this country in the interval between the two world wars.

The British Pottery Industry is well organised both on the employers and employees side. Both sides are represented in the council of the research organisation set up with Government support to tackle the various scientific problems in what is probably still regarded as a typical craft industry. The cordial relationship existing between them augurs well for the smooth development of that increased mechanisation of the industry which is proceeding apace. The term ceramic engineer is not yet one to which English ears are accustomed, but it is a well recognised term abroad, and corresponds more nearly to the modern outlook. In certain processes, mechanisation and instrumental control have to a large extent replaced acquired or allegedly inherited skills, and if they have not altogether ousted the master craftsman they have revolutionised his outlook and mode of operation. It is certain that this process will continue and will affect still further processes which are now considered to be the domain of the craftsman.

The change-over from intermittent to continuous firing has already shown that a higher proportion of first quality goods can be produced by the new methods than by the old, and there is no reason to doubt that a similar experience will result from better control, in other stages of the manufacture once the teething troubles have been overcome.

Illustrations of modern tunnel kilns for firing pottery are shown in Section LXVI.

It must be clearly understood that increased mechanism does not necessarily mean a falling-off in quality. Pride in workmanship on the part of the producer, and pride in possession on the part of the customer, will combine to ensure the maintenance of that quality in design and performance which characterises the best British wares in the price ranges appropriate to the various classes of customer.

Some idea of the present scope of the British Pottery Industry may be gained from Table II., which gives the value of the exports in 1938, 1947 and 1948, taken from the returns issued by the Board of Trade. In 1951–52 exports amounted to £22,000,000. The classification of wares follows closely the commercial organisation of the industry rather than the more traditional one of Knapp, though all the types of ware listed could be fitted into the latter.

TABLE II.

Nature of Ware.	Value of Exports.		
	1938.	1947.	1948.
	(to nearest £1,000)		
I. Glazed wall and hearth tiles	201	1,309	2,329
II. All other tiles	37	67	129
III. Sanitary earthenware, including coloured and cane and white	449	1,320	2,109
IV. Sanitary fire-clay	123	450	576
V. Drainpipes, etc.	72	157	396
VI. China and porcelain	424	2,628	2,913
VII. Electrical porcelain	151	528	849
VIII. General earthenware	2,000	7,139	8,687
IX. Refractory goods	508	1,066	1,419
X. All other descriptions	73	108	217
Actual totals given in H.M.S.O. publication	4,037,953	14,770,188	19,623,324

Other Statistics.—Canadian production of pottery in 1948 amounted to $1,272,108, out of a total of $17,234,475 for all products made from domestic clays. The pottery products (electrical porcelains, and table-, sanitary-, and art-ware) made from imported clays in the same year had a gross selling value at works of $4,508,806. Other products, including refractories, tiles, drain-pipes, high temperature cements, accounted for a further $2,704,934. The number of persons employed was 3,746 in the domestic clays industry and 2,288 in the industries using imported clays.

The production of pottery table-ware (including kitchen-ware) in the United States of America rose from a value of $30,100,000 in 1935 to $65,000,000 in 1943. In the latter year the U.S.A. imported $2,800,000 worth, and exported $1,33[illegible] worth of this ware. These figures are less than one-half and ten times the corresponding figures for 1937, in which year the five major exporting countries exported $33,060,000 pottery table-ware between them. This amount was distributed as follows: Germany, $6,030,000; Japan, $11,880,000; United Kingdom, $10,380,000; Czechoslovakia, $3,770,000; and France, $1,000,000. In the order given the number of employees engaged in producing pottery table-wares were: 41,000, 35,000, 28,000, 16,000, and 18,000. The last figure is also that for this class of ware in the United States in 1937. In the United Kingdom about 40 per cent. only of the total labour force of the pottery industry was employed in the manufacture of table-ware.

The foregoing figures are not strictly comparable owing to differences in classification and other factors.

REFERENCES

(1) United States Tariff Commission, "Pottery Table-ware." Washington, December 1944.
(2) Dominion Bureau of Statistics, Ottawa, "The Clay and Clay Products Industry, 1948."
(3) *Pottery and Glass*, Vol. XXVIII, March 1950.

SECTION LXVI

EARTHENWARE

BY ALFRED B. SEARLE

REVISED BY MARCUS FRANCIS

LITERATURE.—(See under **Pottery**, p. 161)

THE term *earthenware* comprises a large number of different kinds of pottery, all of which consist of a porous body (or biscuit) covered with a suitable glaze. It is sometimes applied to unglazed hollow ware such as flower pots, but it is better to include all unglazed ware under a different term. For domestic earthenware the glaze is essential; without it the ware would become dirty and unsightly in use.

Earthenware may be divided into:—

(*a*) *Coarse earthenware*, composed of a red or buff-burning clay covered with a simple and somewhat crude glaze.

(*b*) *Fine earthenware*, composed of an almost white body covered with a fine glaze, the ware being made and finished in such a manner as shall increase its intrinsic beauty. It is generally agreed that, for the price, there is no pottery better for ordinary use than fine English earthenware, though, when price is unimportant, porcelain has certain advantages.

In the classification of earthenware it is often convenient to group it according to the glazes used, thus:—

1. Ware with a transparent glaze of—
   - (*a*) *Alkaline* nature, as in Persian faience.
   - (*b*) *Plumbiferous* nature, as in most English earthenware and faience.
   - (*c*) *Boracic* nature, as in leadless glazed ware.
2. Ware with an opaque glaze or enamel, as in majolica, Della Robbia and Delft wares. As the enamel usually contains tin compounds as opacifiers, this ware may be termed *stanniferous faience*.

It is, however, desirable to group the various kinds of earthenware according to the composition of the body used, viz.:—

1. *Coarse earthenware* made of a single clay, or of two or more local clays, with the sole addition of sand or crushed pottery. This ware is usually covered with a plumbiferous or an alkali-boracic glaze, and is chiefly used for very coarse pottery, architectural faience (sometimes euphemistically termed glazed terra-cotta), glazed bricks, hearth and wall tiles, sanitary ware, cheap vases and other decorative articles.

2. *Calcareous earthenware* made of marl, or of a mixture of clay and chalk. This is the basis of enamelled ware (majolica, Moorish, Spanish, Delft, Della Robbia ware, etc.). This group of earthenware is largely used for tiles, fireplaces, and for decorative objects. The chalk present is essential to the correct adhesion of the enamel or other glaze used. The glaze is usually opaque, *i.e.*, an enamel, but alkali-plumbiferous glazes, or glazes consisting of alkaline earths and boracic acid, are sometimes used. Calcareous earthenware is not manufactured on a large scale in England at the present time.

3. *Siliceous earthenware*, consisting of sandstone covered with plumbiferous glaze, was made by the ancient Egyptians and Persians, but is no longer manufactured.

4. *Fine earthenware*, consisting of a mixture of fine clays with flint and a felspathic material known as "Cornish stone." The glaze is composed of similar materials, in different proportions, together with various lead and boron compounds.

Many attempts have been made to use glazes free from lead for this purpose, but only with very limited success. There is a considerable field for extensive experiment in this direction, but so far no substance has been found which possesses the same power as lead of producing a rich and brilliant glaze at temperatures suitable to the body of the ware. The number of leadless glazes now in use indicates the great progress made, but the uses of these glazes are very limited, and they lack the brilliance and ease of working possessed by plumbiferous ones in the opinion of many potters.

As previously stated, fine earthenware forms the bulk of domestic, culinary and table ware, and its use for decorative objects is rapidly increasing.

The body of earthenware may be red, yellow, or white according to the clays used. As it is completely covered by the glaze its colour is unimportant, but at the same time, it must be observed that the term earthenware, as ordinarily used, refers exclusively to fine earthenware. The glaze can be scratched by steel and is more readily chipped than porcelain, but is very resistant to changes in temperature.

The better qualities of earthenware are sufficiently dense to "ring" when struck; though the body is highly porous before glazing, it is closer in texture than most of the commoner wares. In appearance and usefulness the best earthenware approaches the ordinary chinawares or porcelains, though the latter, having an impervious body, are preferable for many purposes. Hence, the increased production of cheap chinaware and porcelain tends to displace the use of earthenware for domestic and hotel use.

The Constituents of Earthenware.—All pieces of earthenware are composed of two parts—(*a*) the body of which the article is made and (*b*) the glaze which covers it either partially or completely, and is intended to render it non-porous, cleanly in use and, in some instances, to add to its beauty. A third constituent—the engobe—forms part of some earthenware. The chief object of the potter is to produce a paste from which he may form the body[1] of the articles, this body being required to possess certain characteristics. It must be, for instance, sufficiently plastic to permit its being moulded or worked by hand into any desired shape. When dried carefully it must not twist or warp or otherwise lose its shape. It must also be sufficiently strong not to be damaged by reasonably careful handling. When taken from the kiln it must be strong enough to be employed for all the customary purposes for which it was designed, and it must, therefore, contain sufficient fusible material to bind all the particles strongly together. At the same time, the amount of fusion which occurs must not be sufficient to cause the article to lose its shape. The materials used for the body must be in so fine a state of division that they do not spoil the surface of the ware. Thus, delicate modelling and carving cannot be done satisfactorily if the body contains large grains or gravel like pieces of material. At the same time, it must not be so fine as to make the ware unduly dense, or it will cause cracks. In the crudest and cheapest wares the cost of grinding the material to a very fine state is prohibitive and not infrequently compels the use of coarse clays, to the detriment of the product.

The colour of the fired body must be agreeable for the purposes for which it is to be used. In the case of fine earthenware it must be white, or nearly so. In many instances a body of undesirable colour may be covered with an engobe of a satisfactory nature and the disadvantage thereby overcome.

The glaze must be sufficiently fusible to flow satisfactorily over the surface of the ware to which it is applied, but it must not be so fluid as to run down sloping or vertical portions of the ware, leaving them scarcely covered with glaze.

---

[1] The term *body* is used by potters to mean (*a*) the substance of which the article is mainly composed, *i.e.*, the article itself apart from its decoration and glaze, or (*b*) the paste or other material from which the potter forms his ware. The term is also applied to a thin coating of clay between that of which the article is made and the glaze. It is preferable to use the term engobe for this kind of body (see p. 183).

Too infusible a glaze will be deficient in glossiness, and may contain numerous air-bubbles; too fusible a glaze will be clear and brilliant in places, but it will be unevenly distributed and will be too thin in various parts of the ware.

An *engobe* or *slip* is frequently placed between the body and the glaze. Its sole purpose is to cover the form and to give a finer surface to which the glaze may adhere. On account of its position, an engobe must naturally partake of the properties of both body and glaze, and it usually consists of a mixture of relatively pure clays with some of the glass-forming constituents of the glaze. Engobes are particularly useful when the clay used for the body of the ware is of an undesirable colour, or is of such a nature that the effect of applying the glaze to it is unpleasant. If an ordinary red brick is covered with a transparent glaze, the finished product would always be of a reddish-brown colour. By covering the surface of the brick with an engobe composed chiefly of white-burning clays, however, white glazed bricks can be produced. If coloured bricks are required, the colours may be added either to the engobe or to the glaze. Blue bricks are made by firing red clays under reducing conditions.

This use of a thin layer of superior or more costly clay is generally cheaper and more satisfactory than the use of an opaque glaze—especially if the body of the ware is strongly coloured. It also serves as a convenient means of reducing the cost of the materials used, for large articles may be made of a comparatively cheap clay which, when covered with an engobe, will appear to be made of the superior clay used in the latter. The chief disadvantage of engobes is their liability to spall or crack off on exposure; this can only be avoided by skilful attention to details in manufacture, and on the correct adjustment of the body, engobe, and glaze to each other. It is in this careful adjustment that the remarkable skill of the potter chiefly lies, and it is in this direction also that he derives the greatest benefit from the employment of a skilled ceramic chemist.

When a piece of heated, glazed or engobed ware is cooled, the body, engobe, and glaze will all contract at different rates, and if the stresses developed by these contractions are sufficiently great the ware will be spoiled. The engobe and glaze being very thin, relative to the body, the effects of irregular contraction are most observable in them, with the result that a large variety of defects—cracking, peeling, formation of a wavy surface, etc.—are produced in the glaze.

The differences in the coefficients of contraction of the body, engobe, and glaze are usually very minute, and it requires special apparatus and skill to measure them.

The **raw materials** used in the manufacture of earthenware may be arranged in five groups:—(i.) Clays; (ii.) Fluxes or glass-forming materials; (iii.) Refractory or heat-resisting materials; (iv.) Diluents; and (v.) Colouring materials.

The **clays** used for earthenware differ greatly in character, according to the purposes for which the ware is employed. For the coarsest ware a very low grade clay or brick-earth may be used, but for the finer table ware the clays employed must be carefully selected, and must be free from all impurities which would materially affect their colour when burned. Intermediate between these two types of ware is a large number of others for which a correspondingly large variety of clays may be employed.

In order, however, to keep the subject within limits suitable to the present volume, the nature of the clays used for the coarser earthenware are described under **Sanitary Ware** (p. 207), **Bricks** (p. 213), and **Tiles** (p. 241), the present section being limited to the manufacture of table and decorative earthenware, in which only superior clays are used.

The *blue* or *ball clays* which occur in the tertiary deposits of Devonshire and Dorsetshire form the basis of the finer English earthenware.

These clays vary from a light bluish-grey colour to brown or black when first mined, the colour being due to organic matter. They are peculiarly plastic, unctuous to the touch, and the better qualities are quite free from all gritty matter. These clays occur in the form of an exceedingly stiff paste which is very difficult to cut, and they are, therefore, quarried or mined by a slow process of hand-digging, in which great precautions are taken to prevent dirt getting into the clay. Considerable variations occur in the nature or composition of the ball clays from each quarry or pit, and it is therefore necessary, when purchasing, to state the purpose for which the clay is required. Otherwise, a clay may be supplied which is only fit for the manufacture of common ware or drain-pipes. The firms supplying ball clay can usually be relied upon to make the necessary selection.

When heated to dull redness, a suitable quality of ball clay will become white and very porous, but when heated to a temperature of 1,100° C. or over its colour changes to yellow, sufficient fusion occurs to entirely fill the pores, and the mass, when cold, is so hard that only the hardest steel will scratch it. This yellow tint is detrimental to the colour of the finished ware, and though it is weakened by the other substances comprising the body of the ware, it is usually necessary to add a little cobalt oxide, the blue colour of which optically neutralises the undesirable tint of the clay.

The chemical composition of ball clays as shown by analyses gives very little idea as to their value for earthenware, as a percentage of impurity so small as to be scarcely recognisable on analysis will, in some cases, render a clay quite useless. The following figures are, however, typical of this kind of clay :—

	Blue Ball Clay (Wareham).	Blue Ball Clay (Newton Abbot).	Black Ball Clay (Dorset).
Silica - - - - -	48.99	47.00	52.23
Alumina - - - - -	33.75	38.00	28.25
Lime - - - - -	0.43	1.50	1.30
Magnesia - - - - -	0.22	0.50	0.25
Potash and soda - - - -	3.31	...	1.23
Iron oxide - - - -	1.34	1.50	2.54
Water and loss on ignition - -	11.96	11.50	14.20
	100.00	100.00	100.00

Commercial ball clays usually contain about 18-20 per cent. of water in the form of absorbed moisture, and an additional 12 or 13 per cent. of water is evolved when the clay is heated in a kiln. This latter water appears to form a part of the clay molecule and, on its separation, the clay loses its plasticity and other distinguishing properties. In consequence of the loss of these portions of water, all clays shrink when heated.

The chief purpose of ball clay in earthenware is to form the bulk of the body, any defects in the clay being corrected by the addition of other substances. Thus, flint increases the whiteness of the material, but reduces its plasticity, and it is, therefore, necessary to add a white clay such as china clay, if large proportions of flint are used. Ball clays are so highly plastic that they will stand the addition of very large amounts of non-plastic material such as flint and Cornish stone. Further information on clays will be found on pp. 149-160.

China clays or *kaolins* of good quality are quite white when burned, and they are, therefore, added to ball clays to counteract the yellow tinge of the latter, and also to decrease the plasticity. China clays are the essential constituent of porcelains, and are therefore described more fully on pp. 155, 195.

If china clay enters largely into the composition of a piece of earthenware, the latter will have a more refractory and stronger body than would otherwise be the case, and it would be less affected by sudden changes in temperature. Hence it is a useful constituent of such ware in spite of its peculiar characteristics.

Buff-burning clays occurring near to the works are sometimes added to the body mixture when an inferior grade of earthenware is being made. They serve as an inferior substitute for the ball clay, and usually lower the value of the ware in which they are used.

Red-burning clays used for coarse pottery are closely related to the brick and terra-cotta clays (Sections LXIX. and LXXI.).

Fluxes or Glass Forming Materials.—In order that the articles may be strong when the ware is drawn from the kiln it is necessary that a certain amount of fusion should have occurred, as the fused matter, on cooling, forms a kind of matrix or cement.

When earthenware is made of materials deficient in flux, the ware will be unduly weak and porous, and will not "ring" properly when struck, as its particles will not be sufficiently well bonded together. Many clays contain materials of a sufficiently fusible nature (see **Stoneware**), but in the manufacture of the better qualities of earthenware it is usually necessary to add such a substance, which is then termed a flux.

In the production of *glazes*, fluxes play a highly important part as they form the chief constituents of all glazes and glasses. The chief characteristics of a glaze are that it must melt completely to a glassy mass free from air- and gas-bubbles, and that it must have sufficient fluidity to allow these bubbles to escape, and to permit the glaze to flow uniformly without an excessively high temperature being reached in the kiln. To meet these requirements, it is usually necessary to use a large proportion of flux in the preparation of a glaze.

Fluxes are of two kinds: (*a*) those which are, in themselves, fusible, as glass, Cornish stone, and felspar; and (*b*) those which are only fusible in the presence of certain other materials with which they combine.

Lime is typical of this second kind of flux for, alone, it is practically infusible, yet when mixed with clay it forms a readily fusible material. The chief "impurities" in clay, and most metallic oxides and carbonates, are of this nature.

Cornish stone is a granitic rock, occurring chiefly in Cornwall, which is rich in felspathic material of a sufficiently fusible nature to make it the best flux for the earthenware manufacturer. Its composition resembles a mixture of orthoclase felspar and a highly siliceous clay, but artificially prepared mixtures of these materials cannot be satisfactorily substituted for Cornish stone in pottery manufacture. In addition to this, Cornish stone is somewhat softer than felspar, and can be ground at rather less cost.

Typical Cornish stone shows on analysis—

Potash	6 per cent.
Lime	1 ,,
Alumina	18 ,,
Silica	75 ,,

The mineral varies so greatly in composition that no single analysis adequately represents it. The best method of comparing different samples is to note their colour when fired in a potter's kiln, and also their fusing points and relative hardness or resistance to crushing.

When heated alone, Cornish stone does not fuse sufficiently to lose its shape at temperatures below 1,300° C., but when it forms part of a body-mixture it appears to fuse at about 1,100° C.

Jersey stone and *pegmatite* are other felspathic rocks similar to, but not identical with, Cornish stone.

Felspar is the name given to a number of alumino-silicates of well-defined crystalline form and composition which occur in the older rocks. The felspar chiefly used by potters is that known as *orthoclase*, which is a potash alumino-silicate containing about 16 per cent. of potash, 18 per cent. of alumina, and 65 per cent. of silica.

Calcium, sodium and other alumino-silicates of a similar composition are less fusible than orthoclase and are, therefore, of less value.

Felspar occurs chiefly in granitic regions; that used by British potters is largely imported from Norway.

On prolonged heating, at a temperature of about 1,310° C., potash felspar (orthoclase) melts, but does not form a clear transparent glass unless heated to a higher temperature, or unless mixed with another substance which can lower its melting point. When used in a glaze, felspar gives "depth of tone" and brilliancy, but it is only used to a small extent in the manufacture of earthenware. The colour of felspar varies from green to yellow, but the material usually preferred by potters is a pale yellowish brown or buff.

Nepheline syenite, an aluminosilicate with a smaller proportion of silica than potash felspar, is being used to an increasing extent, particularly in America, where large deposits are found.

Frits are specially prepared glasses made by fusing together various constituents of a glaze (usually the alkali oxides or carbonates and some form of silica or clay) so as to form an insoluble and readily fusible glass.

The use of soluble substances in an unfritted state in a glaze greatly complicates the application of the latter. Many glaze recipes contain the direction to use a stated quantity of "frit"; unless the composition of this frit is stated in the recipe it will be impossible to follow the directions as there are hundreds of different frits (see p. 178).

Borax, or sodium borate (Vol. I., p. 355), is an important source of soda, but all soda and potash compounds have the serious disadvantage of needing to be fritted or fused with other materials in order to make them insoluble before they can be used. When heated alone, borax fuses to a clear glass, but as this is soluble it cannot usually be employed unless it is combined with silica.

Borax is an exceedingly valuable material for reducing the melting point of a glaze and for increasing fluidity and brilliance, so that it is used extensively in earthenware glazes. It should be free from iron and aluminium compounds and from common salt, and, like all the raw materials used in earthenware and porcelain manufacture, it should be tested before use. On heating, borax loses nearly 34 per cent. of its weight of water.

Of the second kind of fluxes (p. 161) *lime*, *magnesia*, *potash*, *soda* and other metallic oxides are so seldom added as such to form body-fluxes in earthenware that for this purpose they may be neglected.

It is, however, necessary to remember that they occur in all clays and that their influence is often sufficiently great to make a considerable difference in the quality of the ware unless the clays are specially carefully selected.

In the manufacture of glazes for earthenware, soda ash and pearl ash (sodium and potassium carbonates) are largely used as constituents of the frit batch.

Whiting, or calcium carbonate, is the form in which lime is usually introduced into a glaze. It is converted into quicklime on heating to about 750° C., but has the advantage over the latter of being insoluble in water.

Alone it is infusible, but when mixed with suitable proportions of clay, silica, alumina and most silicates, it enters into combination and produces a fusible mass.

Its special function in a glaze is to reduce the fusing point, and to increase the durability and clearness.

For some of the cruder forms of earthenware a *marl* (or natural mixture of clay and chalk) is used as a flux. It cannot be employed for fine earthenware on account of the iron compounds present in all marls.

Plaster of Paris (calcium sulphate) (Vol. I., p. 347, also this Vol., p. 121) is sometimes used as a means of introducing lime, but cannot be recommended, as the presence of sulphates is a serious disadvantage.

Baryta (Vol. I., p. 351) is sometimes added to glazes to increase their brillance. It replaces lead whose action it resembles to a lesser extent.

Strontia, *lithia*, and *zinc oxide* are used to some extent in earthenware glazes in order to achieve special effects.

Magnesia and *magnesium carbonate* are used by some potters. They resemble the corresponding lime compounds in their action.

Soda is preferably used in the form of sodium carbonate. The sulphate may be used, but as sulphates are undesirable in glazes they should seldom, if ever, be employed.

Common salt is occasionally used, but is troublesome as it decrepitates when heated. All soda compounds (except soda felspar) must be fritted before use to render them insoluble.

Potash, or pearl ash, is similar in many ways to soda, but generally behaves with greater power notwithstanding its greater molecular weight. It is best used in the form of potassium carbonate, as the less pure form (pearl ash) sometimes introduces too large a proportion of iron into the glaze and stains it an unpleasant yellow.

Potash compounds usually are fritted to render them insoluble but, where the nature of the ware permits, this fritting may be avoided, *e.g.* by the use of potash felspar (orthoclase).

Boracic acid may be used as a substitute for part of the silica when glazes of a very low melting point are required.

Some potters prefer a fritted mixture of boracic acid and soda to the use of borax, though the reason for this is difficult to explain. It is probably due to the fact that a mixture of potash, soda, and lime, or any two of these, has a greater fluxing effect than the same weight of soda.

Lead compounds are invaluable fluxes, as they combine with silica and various alumino-silicates to form a very large number of glazes with a wide range of fusibility.

White lead, or basic lead carbonate, is one of the most useful fluxes known to the potter, as it gives a transparent glaze at a low temperature.

Litharge, or monoxide of lead, is also used as a flux and has similar properties, but being less bulky it is not quite so satisfactory.

Red lead, or minium, is a brilliant red powder consisting of tri-plumbic tetroxide. It fuses at a slightly lower temperature than white lead, but is more dense and is considered to give a yellowish tinge to the glaze.

Galena, or plumbic sulphide, is only used in glazing coarse earthenware as the sulphur and other impurities in this ore prevent its employment in fine glazes. It is the only lead compound which is excluded from the provisions of the Factory Acts for Potteries. This exclusion is due to the great insolubility of galena, which renders it practically non-poisonous.

With this exception, all the lead compounds used by potters are insidious poisons, which are all the more dangerous because their action is so slow and cumulative. Many attempts have been made to avoid the use of lead compounds, but for the majority of earthenware goods no adequate substitute has yet been found. Their use in the raw or non-fritted state is now prohibited by law.

Refractory substances used in the manufacture of earthenware bodies are usually represented by *flint*. This is a concretionary form of silica which occurs in the Chalk formation, and consists of almost pure silica. Such substances must be able to withstand the heat in all parts of the kiln without appreciable fusion; they must be perfectly white after the burning of the ware, and must be used in grains of sufficiently small size not to disturb the uniformity of composition of the body.

Calcined flint is prepared by heating the flints found in the Chalk formation to redness, allowing them to cool in the kiln, and afterwards grinding the product to an exceedingly fine powder. Flints from near Dieppe are deemed of special value for pottery. Calcined flint has a composition equivalent to that of pure silica with up to 5 per cent. of lime and 1 per cent. of other impurities.

Grog or calcined clay is occasionally used for the same purposes as flint, but as it is of the same colour as the clays used in the body, it does not aid in whitening the mixture like a good quality of flint.

Sand, if sufficiently fine and pure, may be used as a substitute for flint as may also Geyserite and Kieselguhr; it is, however, very difficult to get these materials in a high state of purity and fineness. In America sand used in a pottery body is called flint.

Diluents are substances which are used on account of their cheapness. They are not employed extensively at the present time, but may be so in the near future on account of the increased cost of the raw materials now commonly used. Such diluents consist of cheaper varieties of clay, the substitution of some other form of silica for flint, or the replacement of some ball clay and flint by a leaner clay.

Colouring Materials.—These are usually metallic oxides or glasses made from them, and are known in the trade as *stains*. They may be (*a*) mixed with the body of which the articles are made, or (*b*) with a specially prepared body or engobe with which the articles are covered, or (*c*) they may be applied direct to the surface of the article as in underglaze decoration, or (*d*) mixed with the glaze, or (*e*) applied to the glazed article as in overglaze decoration. On some articles the colours are applied in two or more of these ways in order to produce special decorative effects.

The original colour of the "stain" sometimes gives no indication of its appearance when the decorated articles are withdrawn from the kilns, as the final colour depends on chemical changes which occur during the heating of the ware.

The number of different stains on the market is exceedingly large and few potters now manufacture their own stains. In the majority of cases, the stains purchased are mixtures of the colouring oxide with a diluent or some material to effect a desired modification of the tint. Thus, the addition of zinc oxide or alumina to cobalt oxide affects the colour of the latter far more than if it were merely a diluent. In each case, however, the essential ingredient of a colour or stain is a metallic oxide, such as one or more of the following :—

Cobalt oxide gives a strong blue colour. A very small proportion of cobalt oxide added to an earthenware body will counteract the tendency to yellowness, and will make the ware whiter. The use of cobalt oxide for this purpose is precisely similar to that of powder blue by the ordinary laundress in washing household linen, etc. Its action is purely optical and depends on the neutralising power of the blue and yellow colours on each other.

In large proportions—up to 4 per cent.—cobalt oxide colours both bodies and glazes a brilliant blue, the tone of which is made lighter and richer by the addition of zinc oxide or alumina. Cobalt blue is used so extensively in pottery manufacture that many special preparations of it are sold for the production of different shades such as "willow blue," "mazarine blue," "ultramarine blue," "celeste," "sky blue," etc.

Cupric oxide is a black powder used for the production of blues and reds, and is usually added to the glaze or to an engobe of a glaze-like nature. In neutral or acid glazes and an oxidising atmosphere, cupric oxide gives green colours, but in glazes rich in alkali various shades of turquoise blue are produced.

Under reducing conditions and with alkaline glazes, it forms brilliant reds which are usually attributed to free cuprous oxide, but are more probably a highly complex copper-sodium alumino-silicate with some metallic copper. This is the source of the colours known as *rouge flambé* and *sang de bœuf*.

Iron oxide, as used by potters, is a reddish powder of variable composition which, when added to a white body and fired, usually produces a reddish brown or yellow colour, but if there is a shortage of air in the kiln, greenish blue, dark grey, or an imperfect black may be produced.

There appears to be an unlimited number of hydrated ferric oxides, the composition, texture, size of grains, and behaviour of which depend on the manner in which they have been prepared. *Crocus martis*, *ochre*, *sienna*, *rouge* and other iron colours are of this nature.

If the equivalent of about 5 per cent. of iron oxide is present, the ware may be a good terra-cotta red, a much smaller proportion producing a dirty yellow or buff tint. It has been repeatedly shown, however, that the proportion of iron oxide ascertained by analysis bears no definite relationship to the intensity of the colour, and there are good reasons for supposing that the best terra cotta clays do not contain free iron oxide, but some complex compound such as nontronite, which is decomposed on heating, ferric oxide being then set free. The size of the particles of iron oxide also has a great influence on the resulting colour.

In the presence of lime, the red colour ordinarily produced by iron compounds is destroyed, but if the ware is heated almost to fusing point it becomes a pale "bottle-green."

The range of colours produced in earthenware bodies by iron compounds is very great, but great accuracy of tint is almost impossible to obtain. There is room for much further research in this direction.

When added to glazes, the behaviour of iron oxide is quite different from that just described. At temperatures below 1,000° C. a reddish-brown glaze is formed which, with slight reducing conditions, may become purple or black owing to the production of complex ferrous alumino-silicates. At higher temperatures it forms brown glazes, the colour of which is apt to be irregular, but can be made more stable by the introduction of manganese and certain other oxides. With plumbiferous glazes iron oxide tends to form various yellow colours, but becomes green in the presence of an alkaline glaze.

Chromic oxide is usually added to the glaze, as the effects produced with bodies are less pleasing. When fired in a kiln with an ample supply of air, alkaline or simple plumbiferous glazes containing chromic oxide become intensely yellow, but if both alkali and lead are present an orange glaze is produced. If, as may occur in the hotter parts of the kiln, the conditions are reducing, chromic oxide forms beautiful green glazes which are very popular; the simultaneous use of chromic oxide, cobalt and copper enabling a large range of shades to be produced.

In the presence of oxide of tin and lime, chromic acid (or potassium bichromate) forms a brilliant series of tin-pinks which have been extensively used in spite of their true composition being imperfectly understood.

With iron and manganese oxides, chromic acid forms "blacks"—a little cobalt oxide being generally added—but in this connection it must be remembered that there are no true blacks in pottery any more than in the decorative arts generally.

Manganese oxide when added to glazes gives brown colours which are usually more pleasant if both iron and manganese oxides are used. If the glaze is rich in alkali, a violet colour is produced.

Nickel oxide has proved unreliable for earthenware manufacture, but at temperatures of 1,300° C. with felspathic glazes it gives beautiful broken tints of brown and green. The colours produced in the presence of lead and borax are far from pleasing, though when carefully prepared it may be successfully used in the production of some of the newer shades of apple-green.

Lead antimoniate is a bright yellow pigment (Naples yellow) which can be distributed uniformly through any plumbiferous glazes without decomposition. It is the basis of the most brilliant yellows; like other lead compounds it cannot be used at temperatures above 1,200° C.

Antimonic acid in a lead glaze forms the Naples yellow just described.

Uranium oxide produces a number of bright yellow glazes which can be fired at low and high temperatures. It is more expensive than antimony yellow, but can be used under conditions where the latter cannot.

Gold chloride mixed with tin chloride forms *Cassius' purple*, which produces brilliant rose, purple and carmine colours in glazes at temperatures between 850° and 1,100° C.

Metallic gold is applied to the glazed ware in the form of a specially prepared mixture, which is "fixed" by gentle heating in a suitable kiln. The gold may then be burnished by rubbing it with agates, if desired. *Rhodium* brightens the gold.

Other precious metals, such as silver and platinum, are occasionally used to produce a lustrous effect. *Aluminium* powder also yields decorative effects.

Tin oxide (stannic oxide) remains suspended in most transparent glazes, and thus converts them into white, opaque masses resembling some kinds of porcelain. It is the opacifying medium of most white enamels. *Titanium dioxide* is also used.

Tin ash is a stannate of lead made by roasting lead and tin together. It is being rapidly replaced by tin oxide, which is a purer and better preparation.

Zinc oxide and *antimony oxide* behave in a similar, but far less efficient, manner.

Fluorspar, *cryolite*, *alumina* and various other substances are used as opacifying, fluxing or colouring agents, and new preparations are continually being invented.

There is, in fact, a continual demand for new colours in bodies and glazes, and a detailed investigation as to the causes of the formation of several colours is much needed. Many of them are now prepared by purely empirical methods which could, probably, be simplified and improved if the reactions involved were better understood.

Testing Raw Materials.—At the present time very few earthenware manufacturers carry out systematic tests on their raw materials; even the most progressive of them do little more than "run a test batch of ware" when a new supply of material is received. Consequently, there is room for considerable economies and improvements in this direction, though the matter is far more complex than appears at first sight. The tests which should be made must be of a physical as well as a chemical nature, for in many cases variations in the fineness of the material are even more important than in its composition. The fusing points and the speed of reaction with other substances are also matters of importance which are difficult to test precisely.

The influence of apparently unimportant factors, and the difficulty in ascertaining the real causes of various phenomena observed, make the testing of raw materials a tedious task and one which is usually fraught with but small return for the labour spent. Yet this is precisely one of the chief reasons why testing should be systematically carried out, for in no other way can difficulties be overcome or progress made in the industry.

Comparatively small variations in the raw materials used are frequently the cause of very serious losses, so that some examination of all raw materials is absolutely essential to success, if a works is to be well managed on really economical lines.

Earthenware Bodies.—The body of earthenware articles is prepared by mixing two or more clays with sufficient glass-forming material, or flux, to form a material which, when burned, will have a sufficiently close texture, a good ring, and will possess the usual characteristics of unglazed earthenware.

The kind of clays selected for this purpose have been described on pp. 169, 170; the fluxes on pp. 171-172. It is usually necessary to add a considerable proportion of non-plastic refractory material (such as flint) to reduce the shrinkage which the mixture undergoes on drying, and to produce as white a ware as possible. Any tendency to yellowness may be corrected by the addition of a suitable preparation of cobalt.

The proportions of the different materials used differ considerably in different works and according to the kind of earthenware required. In all cases, the *ball clay* is the chief ingredient, and usually forms almost half the weight of the raw materials used. The *china clay* added increases the whiteness of the ware and reduces shrinkage and liability to fracture under sudden changes of temperature. The amount usually present is about half that of the ball clay, but equal parts of each are sometimes used. The larger the proportion of china clay the whiter and better will be the ware. *Flint* is added in quantity about equal to, or rather less than, that of the china clay, and *Cornish stone* to about half that of the flint. A typical earthenware body recipe is accordingly:—

Ball clay - - -	46 per cent.
China clay - - -	23 ,,
Flint - - -	21 ,,
Cornish stone - -	10 ,,
	100

Recipes for earthenware bodies are of small value, for the conditions vary in each works and in the manufacture of each kind of ware, so that each potter has to modify the composition of his mixtures to suit his special requirements.

In practice, the materials are not usually weighed, but are converted into a fluid state by mixing them with water, the required quantities of the *slip* or *slurry* so produced being then measured by volume in order to obtain the mixture desired, at least one modern factory actually weighs the slip.

This arrangement overcomes the difficulty which would otherwise be caused by variations in the proportions of moisture in the different materials, and saves the necessity of determining the proportion of such moisture and allowing for it.

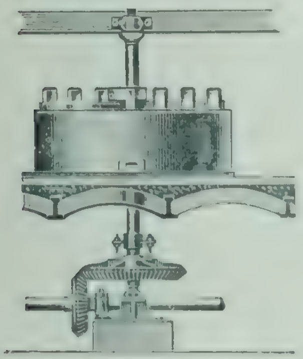


FIG. 1.—Wet Grinding Mill.

(*By courtesy of Messrs T. [illegible] & Co.*)

As it is essential that the composition of the body should be as uniform as possible, all the raw materials must be in an extremely fine state of division. The particles composing the clays are, naturally, so small that no crushing is necessary, but the flint and Cornish stone, and any other materials used, must be ground in mills kept exclusively for this purpose.

In the Staffordshire potteries the grinding of these materials is a trade to itself, the millers supplying both flint and Cornish stone in the form of slips, of which each pint weighs 32 oz. (= sp. gr. 1.6). When this is the case these slips do not require to be constantly blunged, and may be stored in tanks until required.

Each raw material, with a suitable quantity of water, is measured out roughly and discharged into a vertical tank termed a *blunger* (Fig. 2). This machine is fitted with a vertical shaft carrying horizontal blades which, when rotated, effect a thorough mixing of the materials with water producing a creamy slip. This is then run into a storage tank or into a mixing ark, where it is kept agitated.

The thoroughness of the blunging, and the uniformity of composition of the slips, will depend on the correct design and construction of the blungers. These should be hexagonal in shape, and the internal blades should be of such a shape, and set at such an angle, as will give the most thorough mixing motion. It is much better to buy them from a firm of pottery engineers than to attempt to design them and have them made elsewhere.

The blunged material must be tested as to its specific gravity. This is usually done by measuring out exactly one pint of the slip and weighing it accurately. It is important not to have too dense a slip as it will tend to settle too rapidly; too watery a slip, on the contrary, will not mix readily with other slips.

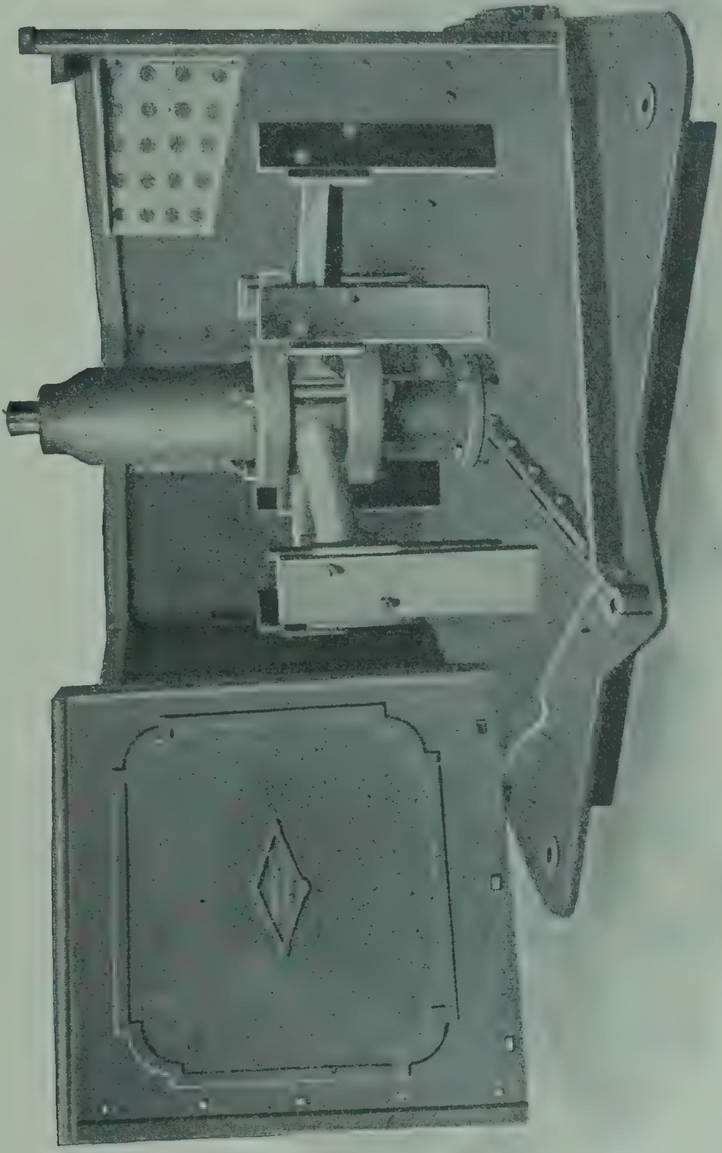


FIG. 2.—Blunger (showing Interior).
(By courtesy of Messrs Wengers Ltd.)

The following pint weights have been found by long experience to be the most generally suitable:—

Ball clay slip	24 oz. per pint.
China clay slip	26 ,, ,,
Cornish stone slip	32 ,, ,,
Flint slip	32 ,, ,,

It is generally desirable to blunge the materials to slips of slightly greater densities than these given, and to make the final adjustment by adding water and again blunging for a few moments, the operations being repeated until the desired "weight per pint" is obtained. As much depends on the density of the slips being accurately known, great care should be taken in this stage of the manufacture.

The various slips, in suitable proportions, are next run into a mixing ark, or light blunger, the quantity of each being usually measured in inches of depth of slip in the ark.

As the sides of the mixing ark are vertical, it is clear that the volumes of the slips added will be proportional to their depth in the ark, and a lath marked in inches and immersed vertically in the latter will serve to measure the volumes with sufficient accuracy.

The order in which the various slips are run into the ark is of some importance; the most satisfactory order is ball clay, china clay, flint, stone and stain. Scraps of body which have been blunged up into slip may also be added, if desired; this is frequently done as it appears to facilitate the working of the body and to increase its plasticity.

The various materials are now mixed together by rotating the blades in the mixing ark—which resembles a blunger—and when a uniform slip is obtained, it is pumped on to sieves termed *lawns*. These usually consist of tiers of rectangular wooden trays, the bottoms of which are made of silk or phosphor bronze wire gauze.

Three lawns are employed, one above the other, the coarsest being at the top. The usual meshes are those known as 14's, 16's, and 18's, but the latter—being very fine—is sometimes omitted. In order to increase the speed of sifting, the lawns are given a "to-and-fro" motion by means of a crank and eccentric. Rotary sieves or sifters are also employed.

The slip which has passed through the lawns is next allowed to flow through a trough containing a number of electro-magnets which retain any particles of metallic iron which may become adventitiously mixed therewith. Efficient permanent magnets are now available.

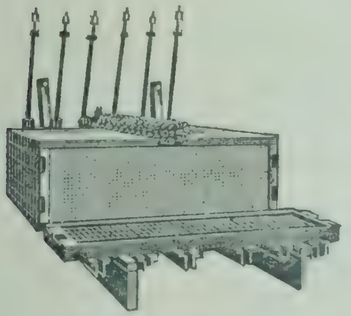


FIG. 3.—Filter Press
(*By courtesy of Messrs T. Willett & Co.*)

Unless these particles are removed, the ware will become yellow and spotty. The magnets must, of course, be cleaned periodically.

The slip is next run into a *finishing ark* where it receives its final mixing before going to the filter presses.

The slip usually weighs about 26 oz. per pint, and so is far too fluid to be used by the potters—even in the process of casting—and must have a considerable proportion of its contained water removed without "unmixing" the other materials. The best means, known at present, for effecting this is by means of a filter press, but the process is clumsy and fatiguing for the workers unless completely automatic presses are employed.

In the filter press (Fig. 3) the slip is pumped into cloth-lined wooden frames which are kept under pressure so as to squeeze out most of the water whilst still retaining the clay. When as much water as possible has been removed, the frames are opened and the cakes of clay are taken out and rolled up. Modern rotary vacuum presses permit man-handling of the press cake to be completely eliminated.

In order to produce a homogeneous mass the cakes are placed in a pug mill which resembles a large sausage machine. In this, the clay is cut, squeezed and mixed until it emerges from the machine in a solid, uniform pasty mass, which is cut into lumps by means of a tightly stretched brass wire and taken to the workmen, or to the clay store, as may be required.

In some works, the older process of *wedging* is still used, the cakes being dashed hard on one another, sliced with wire and the pieces again dashed on each other, this being continued until a uniform paste is obtained. This method is slow and tedious and depends for its success on reliable men who can be trusted not to shirk the hard work involved; except for special work, therefore, it is largely being replaced by the more rapid and, in most cases, equally efficient pug mill. A vacuum chamber is usually incorporated in modern pugs to deaerate the clay body.

Consistency.—There is for each mixture of clays, etc., a definite consistency at which it is easiest to manipulate, and the potter must, therefore, take care that the correct amount of water is present in the pugged paste.

If too much water is present, the body will be too soft and adhesive, whilst if it is too dry it will not fit well into the moulds and will fall to pieces during later stages of manufacture. The consistency which is generally suitable is that at which the clay paste is sufficiently soft to be easily worked into any desired shape without it adhering to the fingers of the workman. An experienced potter can immediately tell by the "feel" of a piece of clay paste whether its consistency is what he desires.

The chief property possessed by all earthenware bodies of being capable of formation into any desired shape by the mere pressure of the fingers is termed *plasticity*. Little is known at present of the causes of plasticity, but it is a characteristic of most clays and is one of the most important distinctions between them and other substances. Further information on the subject will be found in the section on **Clays** (p. 149).

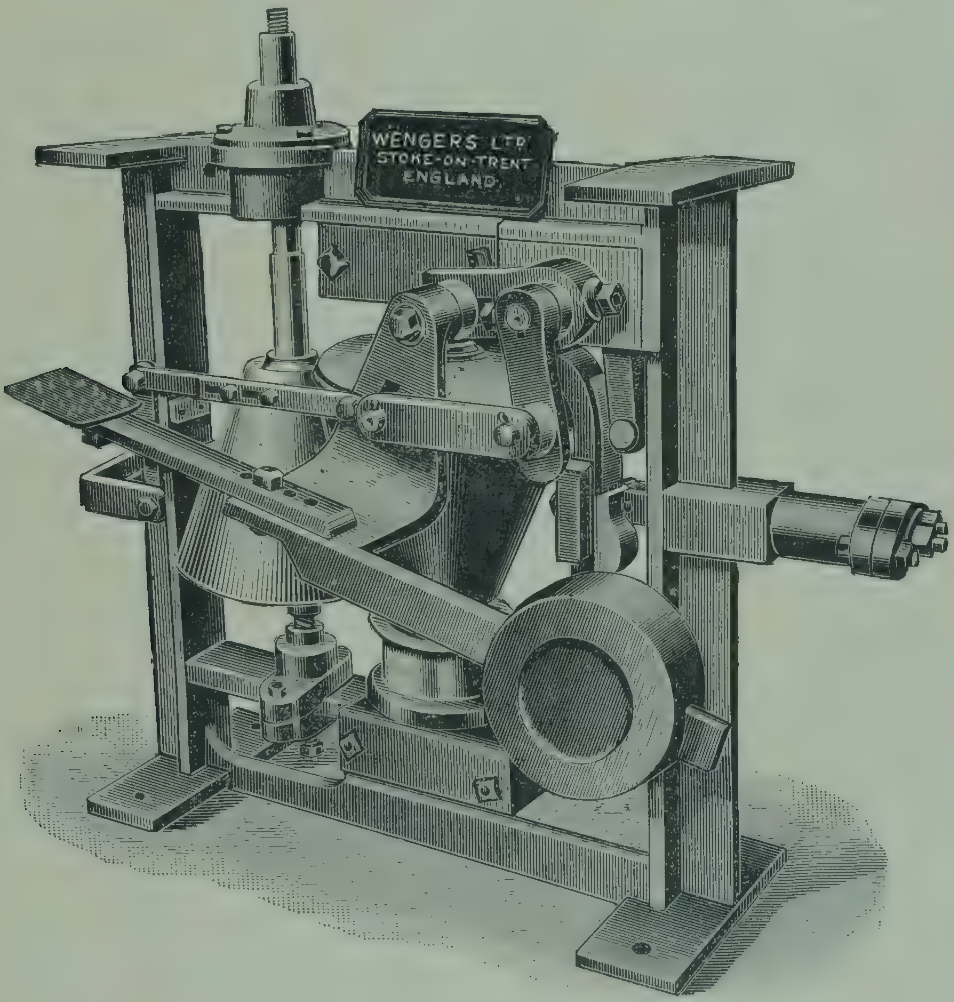


FIG. 4.—Potter's Wheel (Power-Driven).
(*By courtesy of Messrs Wengers Ltd.*)

Methods of Shaping Ware.—In the production of earthenware, a number of processes may be used singly or in combination according to the articles to be produced. The most important of these methods are as follows:—

Modelling, which consists in giving a pasty mass of body the desired shape by cutting, pressing, and pulling portions of it. This is, in some ways, similar to the work of a sculptor in carving stone, but the greater softness and plasticity of the body enables the fingers and small wooden tools to take the place of the sculptor's hammer and chisel. Moreover, pieces of fresh paste can be added to the main mass whenever desired—a property that is only possessed by plastic substances.

Modelling is only used when a single article is to be made, or when a mould is to be produced. It is slow and somewhat tedious work, even when ample facilities are provided, but it is the starting point of practically all methods of manufacture.

Throwing is a special form of modelling in which the potter uses a rotating plate—the well known "potter's wheel"—on which to form the article. The earliest wheels were simply flat wooden discs mounted on an upright spindle and kept in motion by occasional blows administered by the hands or feet of the potter, but the modern wheels are more complex and driven mechanically or electrically (Fig. 4).

In making symmetrical articles, such as vases and most domestic vessels, the use of a wheel greatly facilitates the shaping of the mass. The potter dashes a pasty lump of body onto the wheel and starts the latter rotating. He then wets his fingers in a bowl of water and applies them to the mass in such a manner that it rises and falls in a conical shape until it is well mixed and free from air-bubbles. He then forces his thumbs down on the centre of the mass, and with his fingers converts it into the desired shape, the final touches being given with various small tools made of wood, horn, or metal. The surfaces are then cleaned with a wet sponge, the article is cut from the base, by means of a stretched wire, and passed on to the next workman.

Throwing is skilled work and many precautions must be taken by those engaged in it, but these need not be mentioned here. It is sufficient to state that an incompetent thrower may produce articles which appear to be quite satisfactory when they leave his hands, though at a later stage they become twisted and warped through irregular strains and pressures applied by the thrower.

Many vessels may be finished by the thrower, but if great accuracy of shape is desired it is usual to have them "turned." Unfortunately, throwers are being displaced by mechanical contrivances (presses) which produce similar results more rapidly and cheaply, though with less artistic value than those possessed by articles thrown by a clever potter.

Articles of complex shape are sometimes thrown in two or more pieces which are afterwards joined together.

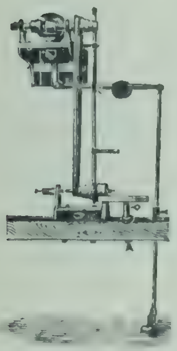


FIG. 5.—Lathe.

(*By courtesy of Messrs T. Willett & Co.*)

Turning is a modification of throwing, and consists in treating the dried piece of ware on a lathe in a manner precisely similar to that employed by engineers in turning wood, steel or iron to a desired shape. The chief difference is that the green body is so soft that very little power is needed for driving the lathe, so that a small treadle-lathe or low power motor is generally used.

The turner is usually supplied with ware which has been "thrown" to almost the desired shape, and his work consists chiefly in finishing the ware, and giving it an accurate shape. In the manufacture of electrical fittings the degree of accuracy required is sometimes almost as great as that for metal, notwithstanding the great differences in the materials used.

By means of special attachments to the lathe, elaborate devices may be turned with ease and rapidity, and the demand for accurate and complex ware is such that much of the ware made mechanically in presses, etc., is now finished by turning it on a lathe. The finish given by turning is better, and the shape is more accurate than those obtainable by any other process of shaping except grinding after firing. A crude form of turning is used for rough pottery, and is known as *fettling*.

Moulding is now the most usual method of shaping earthenware articles. The paste is placed in suitable moulds made of plaster of Paris, and is pressed into them either by hand or by some mechanical means, the surplus material is removed, and the mould is then set aside to dry. After some time, the contents are taken out and a replica of the article or model is thereby produced.

For some complex articles, the moulds must be made of many parts, but the principle is the same.

Potters do not usually employ the term "moulding," but include this operation under "pressing," even though no presses are used.

The simplest form of moulding is when the paste is pushed well into every part of the mould by hand, and after the article has been removed from the mould its surface is finished as may be required. This process is used for all articles which cannot be made on rotating machines.

An ordinary ewer, or jug for toilet use, is typical of the kinds of ware which are made in moulds. For plates, etc., the mould consists of a single piece, but for most hollow ware it is made of at least three pieces, the handle being made in a separate mould and attached later. The inside of the moulds is sponged with clean water, and the various parts are filled separately with a flat cake or bat of body, which is somewhat larger and rather thicker than the portion of the ware to which it corresponds. The body is carefully pressed well into the mould, and any excess is carefully removed. The various parts of the mould are now fastened together, and the "joints" or spaces between each piece of body are carefully obliterated by working with the fingers, more body being added if necessary. When the various pieces of body have been properly united, the inside surface is trimmed to shape with a small scraper, and is finished with a sponge and clean water, until it is as smooth as possible. The mould with its contents is then set aside until the body is sufficiently stiff for the mould to be emptied with safety. After this, the article is trimmed externally, the handle is attached by means of a little body slip, and the whole surface of the article is then finished with a wet sponge and a piece of leather or linoleum until it is quite smooth.

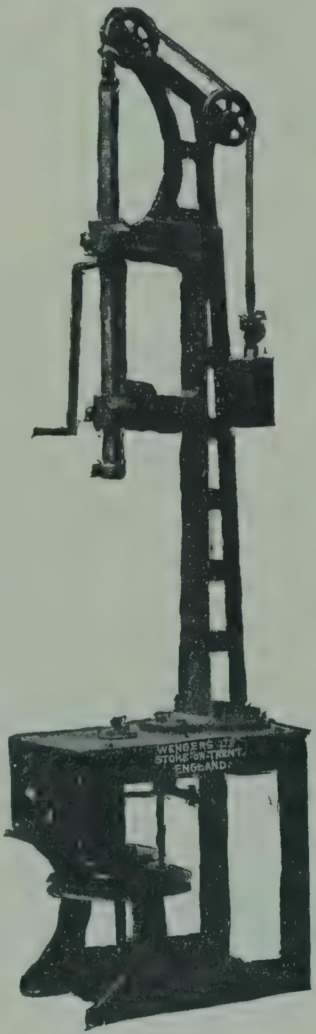


FIG. 6.—Vertical Jigger and Jolley.

(*By courtesy of Messrs Wengers Ltd.*)

The article is then taken to the "stove" or drying chamber.

Each workman will require a large number of moulds to keep him fully occupied.

The moulds soon become "sick," and will not deliver the ware properly; they must then be cleaned by carefully scrubbing the interior with a wet brush. If this and a thorough drying does not revive them, they must be discarded.

Jolleying is a form of moulding which is more rapid and requires less skill than hand pressing. The jolley consists of a mould fitted on to a kind of potter's wheel (Fig. 6), and the lump of body is thrown into it. A piece of pottery, wood, or steel—termed a profile—attached to a suitable framework—termed a jigger—is then brought down on to the paste, and the pressure it exerts, in combination with that of the rapidly rotating jolley, rapidly confers on the lump of body the desired shape.

Jolleying is, therefore, a combination of processes whereby the exterior shape of the article is moulded, and the inside is simultaneously turned. This process is sometimes reversed, as in the manufacture of plates, which are made upside down, the profile forming the "bottom" of the plate, and the mould the face or interior. It is then called *jiggering*.

It is often convenient to use two machines, one to form a flat disc or *bat* of paste, and the other to give this the final shape desired.

Presses of various patterns are used for wares required in large quantities, the most usual form for earthenware being a jolley or jigger. For hearth tiles and other wares not readily formed by jolleys and jiggers, toggle-levers or screw presses (Fig. 10) are largely employed. These presses are provided with metal moulds consisting of two chief parts—the *box* which is attached to the bed of the machine and the *plunger*, or moving part, which fits into the box. A suitably sized lump of paste is placed in the box, and the plunger brought down forcibly by means of the mechanism provided. The body, being under great pressure, is thus made to occupy all the interstices in the mould, and any excess of material is forced out through an escapement. On reversing the machine, the plunger is raised and the article may then be taken out of the mould. Very complicated pierced shapes may thus be made from moist dust.

As these metal moulds are costly, the use of presses is limited to wares which are required in large numbers, such as tiles or electrical porcelain fittings. The more complicated the shape to be pressed the more plastic the body needs to be; hence, electrical porcelain parts are pressed at a higher moisture content than, say, white wall tiles which are pressed from dust at about 10 per cent. water content.

Casting is a form of moulding which is specially suitable for very thin ware, though in some instances it may be used for thicker articles. The moulds used for this purpose are of plaster, and a body slip—carefully lawned to free it from grit—is poured gently into the moulds. The plaster absorbs most of the water from the slip, and after a short time the mould is inverted, any remaining slip is poured out, and the mould is left for the body within it to dry and shrink. This does not take long, and the body can then be taken out of the mould in the form of an article which usually requires retouching or sponging.

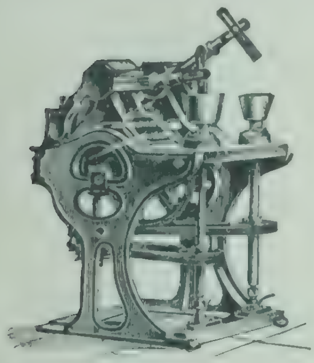


Fig. 7.—Automatic Cup-making Machine.

(*By courtesy of Messrs T. Willett & Co.*)

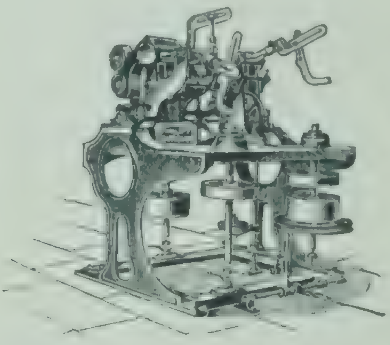


Fig. 8.—Automatic Machine for making Wash Bowls, etc.

(*By courtesy of Messrs T. Willett & Co.*)

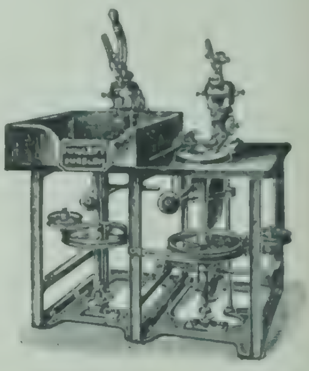


Fig. 9.—Plate-making and Batting Machine.

By courtesy of Messrs T. Willett & Co.)

For successful casting the slip must be very fluid, but must contain only a little water. The addition of a small percentage of carbonate and silicate of soda to the clay reduces the proportion of water needed to make the slip fluid by 40-45 per cent. Organic deflocculants may also be used.

Cast ware is very porous, and shrinks greatly on drying; it is more largely used for porcelain than for earthenware, though there are many earthenware articles, such as spouts for tea and coffee pots, which cannot be made so easily in any other way. This method is also of special value for thin ware of a complicated pattern.

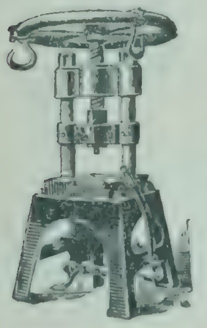


Fig. 10.—Screw Tile Press.

(*By courtesy of Messrs T. Willett & Co.*)

Expression of the body through a die or mouthpiece fitted on to the exit end of a pug mill is only used for the cheaper handles and similar solid parts of articles. In the manufacture of bricks and tiles, on the contrary, this is one of the most important methods of manufacture; it is described in the section on **Bricks** (p. 213). This process is also known as *extrusion.*

Finishing.—There are a number of minor processes through which the articles must pass before the shaping can be considered to be complete. The surface may be *scraped* and *polished* in order to remove blemishes; some portions may require to be *carved* or *undercut*; others must be *repaired* by the addition of a little fresh body followed by gentle trimming and polishing.

Slipping and *sticking up* are terms employed for fastening handles, feet, spouts, and other accessories on to articles; it is generally advisable that distinct projections such as these should be moulded separately, and afterwards stuck on to the article; to mould the whole at once greatly complicates the manipulation, and prevents the ware being made so satisfactorily. *Sticking* consists primarily in moistening and pressing together the two parts to be joined, or uniting them by working in a small roll of plastic body. *Slipping* is used for less plastic bodies; it consists in covering the surfaces to be united with body-slip and then pressing them together.

Engobing consists of the application of a coating of a body different from that of which the article is made. Thus, earthenware articles may, for the sake of cheapness or for some special reason, be made of a body whose colour, when fired, is undesirable. Such a body can be covered with an engobe of superior clay, and in this way can be made to resemble first-class earthenware.

Engobes are, usually, of the same composition as the best earthenwares, but it is sometimes convenient to add a little extra flux or glaze to them, in order to increase their adhesion to the body of the ware. Where a coloured engobe is required, the appropriate stain (p. 173) is added to it before use. They are applied in the same manner as glazes, but occasionally the engobe is placed in the mould in which the article is to be made, and the coarse material is then used to form a "backing."

Drying Earthenware.—Owing to the large amount of moulds and of space which would otherwise be occupied, and the necessity of avoiding draughts, it is almost imperative that some form of artificial drying should be employed, and *drying stoves* are generally used for this purpose. Each mould must be dried before its contents can be removed, so that the stoves must have ample capacity for all goods that each maker can produce. Many stoves now in use will hold a thousand or more moulds. Novel designs have recently been introduced using forced air circulation.

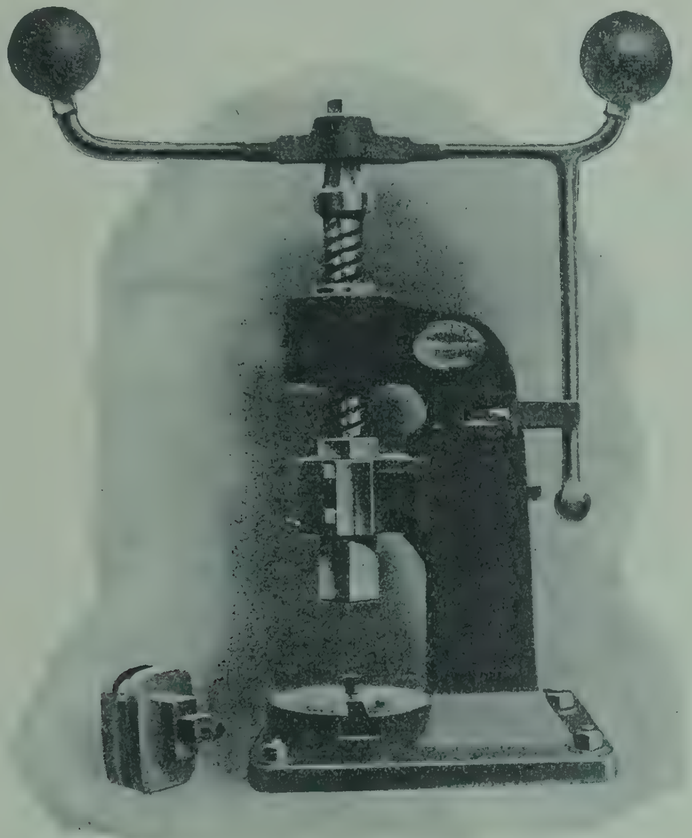


FIG. 11.—Screw Press for Small Ware.
(*By courtesy of Messrs Wengers Ltd.*)

The ordinary drying stove for fine earthenware consists of a series of shelves about 10 ft. high and 12 ft. square, arranged on the axes of a hexagonal frame (Fig. 12) with just sufficient space between each shelf for it to accommodate the moulds. The frames carrying these shelves are mounted on vertical shafts so that they can be rotated slowly. They are enclosed in compartments which are heated by steam or hot-water pipes near the floor, several frames being placed in each compartment. Opposite the centre of each frame there is a door of just sufficient width to enable the moulds in one arm of the frame to be put on or removed, as desired. The use of an enclosed stove of this pattern, with a narrow doorway, enables the heat to be used to the best advantage, whilst also allowing ready access to all the goods in the stove.

For very large articles fixed shelves around the walls of the drying room are generally employed.

When the articles in the moulds are sufficiently dry they are removed, placed on a revolving table, termed a *whirler*, and carefully sponged or rubbed with a piece of leather to give them the necessary finish. Wares of a specially fine nature sometimes receive a further polishing by means of flannel or tow, applied to the almost dry body. If necessary, they are replaced in the stoves and the drying completed.

The finished goods are then ready to go to the kilns or ovens. Plates are placed in bungs consisting of twelve plates placed one above the other.

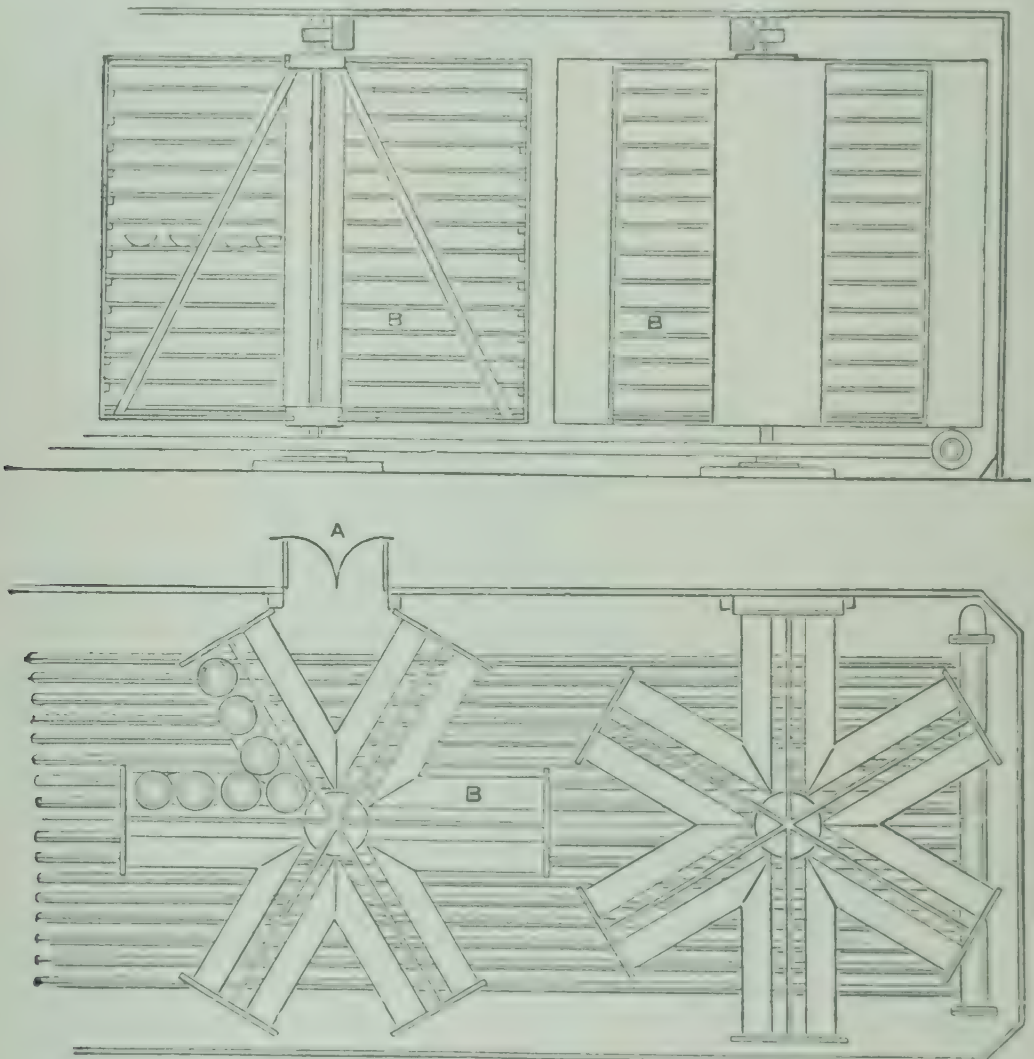


FIG. 12.—Section and Plan of Drying Stove.

Shrinkage.—During drying, the water present in the pasty body is removed in two ways: (*a*) by absorption by the plaster, the pores of which are too fine to allow the clay to pass through them, and (*b*) by evaporation. In each case the removal of the water produces a reduction in the size of the articles, and allowance must, therefore, be made for this shrinkage. The amount of contraction differs with different bodies, but is usually about one twelfth of each dimension of the article, except in cast ware in which it may be much larger.

Bodies with a high shrinkage on drying usually have a strong tendency to warp and crack, so that it is desirable to keep the shrinkage as low as possible. This may be done by substituting china clay for some of the more plastic clay or by the addition of flint. A certain amount of plastic clay is, however, essential; without it the particles cannot be kept together. Hence, all articles made from a plastic body invariably shrink during drying.

In small, thin pieces, the shrinkage and drying do not usually present great difficulties, but in larger and thicker ware the greatest possible care is needed, and the drying must be exceedingly slow.

Further information with respect to shrinkage will be found in the section on **Clays** (p. 149).

Ovens.—For burning earthenware, round vertical kilns, or *ovens*, are chiefly employed. In shape they resemble a large, but stumpy, bottle, and consist of a cylinder of brickwork about 8 ft. 6 in. high, above which is a high dome surmounted by a chimney. Around the circumference of the oven is a number of fireplaces, the flame and gases from which enter the interior of the oven and pass partly up small chambers or *bags* and amongst the contents, and partly down through the floor or *sole*. Both sets of flame and gases eventually rise up through the kiln and finally pass out through the chimney at the top.

Sometimes the oven proper is quite independent of its chimney. The latter is then built in the form of a large bottle-shaped structure which completely surrounds the kiln and is termed a *hovel* (Fig. 15).

This arrangement prevents the wind from blowing the fires and so disturbing the heat of the oven: it forms, however, a very hot and confined space in which the firemen work and the draught is liable to be feeble and irregular.

Down-draught ovens (Fig. 16, p. 229) have long been used on account of the even temperature which can be produced in them. They are of various patterns and often differ considerably in their constructions, but in all cases the flame and hot gases from the fuel first rise up inside the walls of the oven until they reach the dome; they are then turned downwards and, passing through one or more openings in the floor of the oven, they travel through a series of flues to a separate chimney.

In order to economise fuel, two ovens are sometimes built on top of each other (Fig. 14), the waste gases from one then passing into the next oven. This form is normally used for firing continental or hard-paste porcelain, the lower part of the oven being used for the glazed ware, the upper part for the biscuit or dégourdi. The firing temperature of the lower chamber is much the higher of the two.

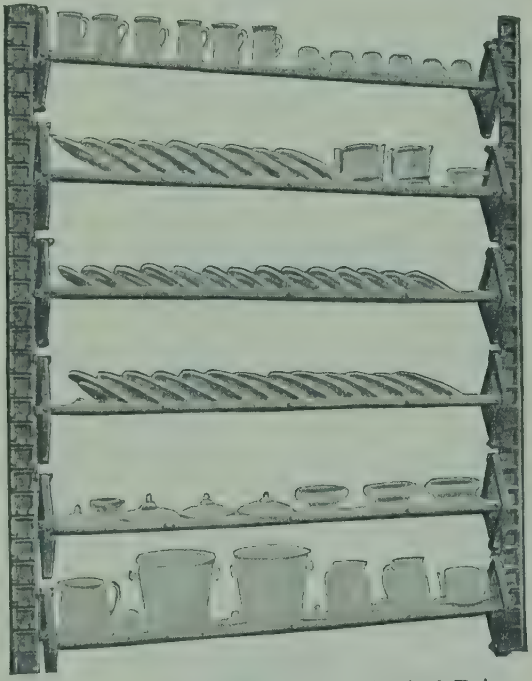


Fig. 13.—Movable Shelves in Vertical Drier.
(By courtesy of Messrs T. Willett & Co.)

Many attempts have been made to use tunnel ovens into which the goods are introduced at one end, heated slowly until they reach the centre of the oven—where they attain their highest temperature—and then cooled gradually until they pass out at the further end (Fig. 16).

As might have been expected, kilns for the lower temperature range required by gilding, on-glaze decoration, etc., were the first to become well established. The first successful tunnel kiln for glazed earthenware in the Potteries district was erected round about 1910. This was working until comparatively recently.

Progress has been steady, despite the two world wars and the depression in between, and the excellent results achieved with the newer designs of tunnel oven have convinced the industry of their value, so that the days of the old-fashioned bottle oven now appear to be numbered. The process of conversion has been accelerated by the discovery that the thermal efficiency of the kiln does not necessarily increase with the size, as was at first believed, and there is a tendency for even the large-scale manufacturer to build several smaller kilns instead of one colossus. Greater flexibility is thus achieved and one of the main objections to the large tunnel oven removed. Gas and electricity appear to be the generally preferred heating agents in Britain, owing to their convenience and cleanliness. Round kilns are useful where spatial considerations rule out the straight tunnel. Various mechanisms for moving the goods have been adopted, including a continuous wire mesh belt in some of the latest, small, glost kilns. There is an obvious temperature limit to this type of transport.

Other forms of continuous firing, *e.g.*, the Shaw kiln—somewhat similar to the Hoffman—hav not taken on well, though from the thermal efficiency standpoint they compare favourably with the tunnel kilns. Similarly, the rotating platform continuous kilns represented in Britain by th Woodall-Duckham, are confined to a few specimens for biscuit or glost temperatures, though they are much more popular for enamel kiln work owing to their compactness.

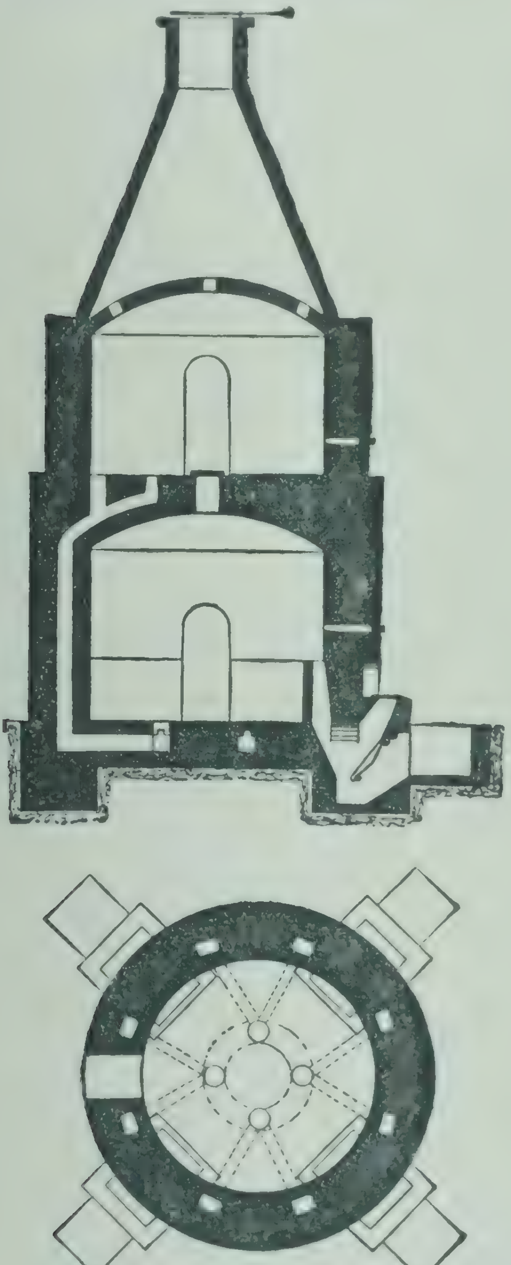


FIG. 14.—Vertical Section and Plan of two-tier Porcelain Oven.

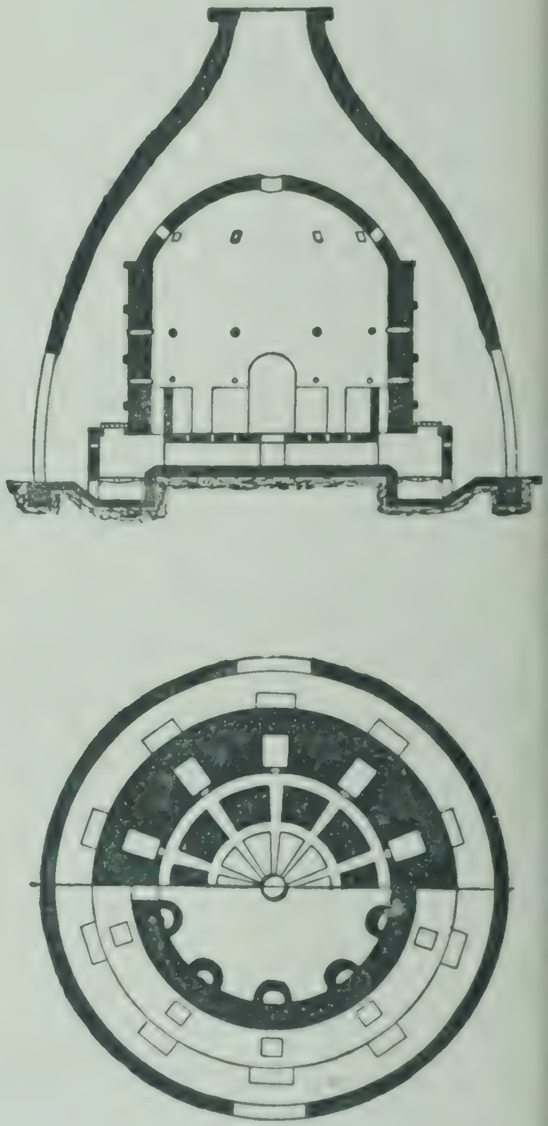


FIG. 15.—Vertical Section and Plan of Hovel Oven.

Setting or **placing** are terms used for what, in less technical language, would be designated as "filling the oven." The earthenware is first placed in oval or round boxes made of fire-clay (termed saggers), and these are then piled one on top of the other until the oven is "filled."

The earthenware is so tender that it requires great skill and care to place it properly in the oven. A single sagger full of plates is a heavy and difficult article to manipulate, especially as many of them have to be carried up ladders in setting intermittent ovens.

Biscuit or unglazed ware is easier to place because the pieces can be laid on each other so long as there is not too much weight on any portion of the ware. The skill of the setter in biscuit placing consists, therefore, in placing the largest quantity of ware in the kiln.

In placing glazed ware, or *glost*, the glazed surfaces must, as far as possible, be kept out of contact with any other surface, and the ware is therefore supported on "pins," "spurs," "thimbles," and other specially shaped pieces of fire-clay, the sharp edges or points of which are designed not to spoil the appearance of the glazed surface of the ware.

Much ingenuity has been exercised in devising means of placing glost ware in saggers; detailed descriptions of these devices are given in Bourry's "Treatise"[1] and other technical works.

The number of saggers in an oven is very large, being usually above 2,000. They are arranged in a series of *rings*—usually five—and are piled on one another until the oven is filled. Sufficient space must be left between the piles or *bungs* of saggers to permit the proper circulation of the fire gases.

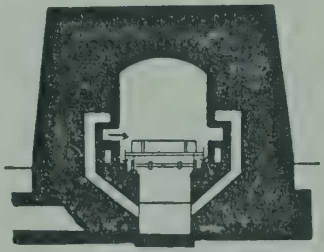


FIG. 16.—Cross Section of Tunnel Kiln.

To prevent the flame entering the saggers and discolouring the ware, they are luted with sand or clay—preferably the latter. The lute also affords a means of properly bedding the saggers on each other; if this is done carelessly the loss resulting from the breakage of saggers will be serious.

Firing.—The firing of earthenware biscuit requires great care and skill. It is necessary to heat steadily and slowly, so that the water evolved on the decomposition of the clay may not escape too rapidly and so damage the ware. The ware shrinks as the water is removed, and if the heating is irregular the ware will twist and warp to such an extent that it becomes useless.

This second, or kiln shrinkage, is only about one-third of that on drying, but if the rate at which it occurs is excessive the possibilities of damaging the ware are very large.

The temperature finally attained in the biscuit oven is about 1,200° C., the ware being heated until it has attained the desired hardness and density rather than to any definite temperature. Some potters find it better to heat for a long time at a somewhat lower temperature, others prefer a higher temperature and a shorter heating.

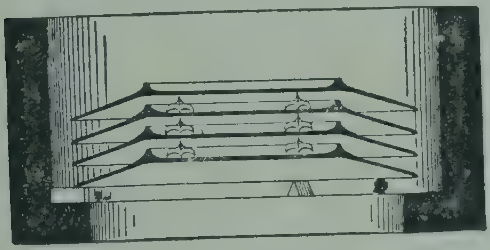


FIG. 17.—Plates in Sagger.

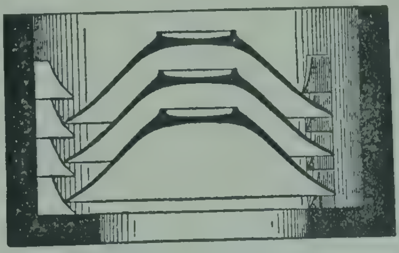


FIG. 18.—Basins in Sagger.

Trials made of pieces of earthenware, are placed in convenient parts of the oven, and are drawn out through special trial-holes. By drawing out trials at regular intervals from various parts of the oven, the extent of the action of the fire on the ware can be ascertained. Various pyroscopes—including the very ingenious shrinkage-gauge of Wedgwood and the Seger cones (Vol. I., p. 539)—are also used for ascertaining when the firing of the ware is likely to be finished.

Skilled firemen can judge the temperature of a kiln by looking at it carefully, and when accidents have happened and part of the inside or contents of the kiln have slipped, the fireman is frequently compelled to rely entirely on his experience of the "colour" of the kiln to enable him to finish the burning.

---

[1] Figs. 12, 14, 15, 17, and 18 are from Bourry's "Treatise on Ceramic Industries."

In order that the ware may be burned economically, the fireman must heat it as rapidly as is consistent with safety, and in order that the heat may be uniform he must carefully regulate his fires and the quantity of air admitted. The coal used should be long flamed and of fairly good quality; it costs more to use a poor coal than a better one on account of the longer time needed for heating.

There are many opinions as to the best methods of heating ovens for earthenware biscuit, but the most satisfactory ovens are those in which the temperature is raised steadily until the finishing point of the ware is reached, and in which this temperature is maintained as long as may be necessary. Flat ware, such as plates, dishes, etc., requires a long time to gain the temperature of the oven, and holding the fire at the finishing temperature—a process technically known as *soaking*—is almost essential. Soaking at a temperature much below the finishing point is almost useless with earthenware.

For thirty hours, the oven requires little attention beyond steady firing, but, about twelve hours before the end, difficulties commence. The most critical time of all is the last firing or *baiting*; at this point the temperature must be raised with great care, and the indicators, trials, etc., must be very carefully observed.

When the firing is finished, the oven is luted up and left for at least twenty hours so as to cool uniformly. After this it may be partly opened, and when cool enough it is *drawn*, *i.e.* emptied. The product is biscuit or unglazed earthenware; it must usually be glazed before use.

Glazes.—In the manufacture of earthenware a glaze or glassy covering is essential, as the body of the ware is porous, and easily becomes dirty. Earthenware glazes are fired at a somewhat lower temperature than the body, but very soft glazes fired at an exceptionally low temperature are undesirable, as they are very liable to crack and peel off, and are apt to be poisonous because of the soluble lead salts formed in contact with liquid food-stuffs. Readily fusible glazes which are free from lead have not, as yet, proved universally satisfactory.

As already noted (p. 170), the glazes used for earthenware are chiefly composed of some of the following: borax, soda, potash, china stone, flint, whiting, china clay, and one or more lead compounds. As some of these substances are soluble in water, they could not be used in the ordinary methods of applying the glaze to the ware (*i.e.*, by dipping), and such substances must, therefore, be converted into insoluble ones. This conversion is affected by fusing certain ingredients of the glaze together, thus forming insoluble silicates, alumino-silicates or boro-silicates, according to the substances present. This process is known as *fritting*, and the fused product is termed a *frit* (p. 172).

The following are typical mixtures for making frits for *earthenware glaze*:—

MIXTURES FOR FRITS.

	A	B	C	D
Borax	30	36	39	24[1]
Cornish or china stone	30	20	23	21
China clay	5	6	7	10
Flint	15	20	18	20
Whiting	20	18	13	14
Soda ash	...	...	...	11

The frit mixture is placed in a reverberatory kiln and, when fused, is run into water which granulates it. If the granulation is properly effected there is no need to grind the frit before preparing the glaze.

Earthenware glazes are usually made of the following ingredients mixed in proportions similar to those stated on the next page:—

---

[1] Boracic acid.

MIXTURES FOR GLAZE.

	A	B	C	D
Frit	50	36	58	55
Cornish stone	25	40	16	25
White lead	25	24	22	20
Flint	...	..	4	...

The glaze or tub-mixture is ground with water to an extremely fine powder in a ball-mill, Alsing cylinder or chert-lined mill, and is carefully sifted through *lawns* of silk or phosphor bronze. It is then run into a blunger, the arms of which are fitted with electro-magnets so as to remove any adventitious particles of iron, or these particles may be removed by running the glaze-slip through a trough fitted with powerful magnets.

It is necessary to adjust the composition of the glaze accurately if the best results are desired, and this is all the more important as glazes do not appear to be definite chemical compounds, but are of the nature of one solid dissolved in another ("solid solution"). If conditions are favourable, crystals of definite compounds will form in the glaze, but as these destroy its value, the glaze maker is careful to avoid forming such crystals in ware intended for domestic use.

The effect of the various ingredients on each other has already been mentioned (p. 162), and their constitution and composition are so complex as to form one of the chief subjects which a ceramic chemist must study. Usually, the greater the proportion of metallic oxides or of boracic acid or borax in a glaze, the lower will be its melting point, but much depends on the nature of the other constituents. White lead is the chief and most useful flux employed by potters in the production of earthenware glazes, and though many attempts have been made to avoid its use this has only proved possible when the glossiness or some other important characteristic of the glaze has been partially sacrificed. The use of barium compounds has proved valuable, but not sufficiently so as to enable the use of lead to be discarded. Under recent legislation it is no longer permissible to use "raw" lead glazes in pottery manufacture: the lead must be made harmless by conversion into an insoluble form, *e.g.*, a silicate.

Glaze is applied to earthenware which has been fired (biscuit) by dipping the article into the glaze slip. The earthenware is porous and absorbs the water in the slip, leaving the article covered with a thin coating of glaze mixture. Mechanical appliances are sometimes used, but for all but the simplest shapes handwork is better.

The ware is allowed to dry and is then taken to the kiln, placed in saggers, and fired until the glaze has fused to a uniform glassy covering. Any support coming in contact with a glazed surface will spoil the latter at that point, and it is therefore necessary to keep these points of contact as small as possible (see "Setting").

During the second heating in the kiln—which is known as *glost-firing*—the materials forming the glaze fuse to a molten glass and combine sufficiently with the body of which the ware is made to form a strongly adhesive and impervious coating. If this coating, or glaze, has a coefficient of expansion appreciably different from that of the body, strains will be set up in both body and glaze, and the latter will crack or peel off. Ordinarily, glazes are transparent, but opaque glazes (enamels) are sometimes used in the production of white ware from a coloured body. The usual opacifying medium is oxide of tin.

The kilns used for firing glazed earthenware are of the same type as those used for burning earthenware biscuit, but a lower temperature is required for the glaze.

THE DECORATION OF EARTHENWARE

The decoration of earthenware may be effected in various ways. The body of the article may be modelled, carved, or moulded so as to form an attractive design. Coloured clays may be used to form some portions of the article, or designs may be "painted" or sprayed on the ware with suitable pigments. Where large quantities of ware with the same designs are required, it is customary to mix the colours with a special oil, then to use this mixture to print the designs on suitable paper and to transfer it to the ware. This is known as "printing."

The application of the colours may be made (*a*) to the body and below the glaze—*underglaze* decoration, (*b*) in the form of a stained glaze (p. 173), or (*c*) to the glazed earthenware—*overglaze* decoration.

Of these, the first is the most permanent, as the design is completely covered by the glaze, and the overglaze decoration is the least durable because it is on the surface of the ware.

The colours used for underglaze decoration are more limited than those for overglaze work, because the former must resist the temperature and conditions of heating produced in burning the biscuit and glost ware. The overglaze colours, on the contrary, can be fired at any temperature which may suit them, and the widest possible range is thus obtained.

For underglaze painting the colours are finely ground, and mixed with turpentine or with gum arabic and water. They are then painted with brushes, or with small pieces of sponge cut to a convenient shape. The colour is "dabbed" rather than painted, and as there is no definite relationship between the colour, as used, and that which is seen when the ware comes out of the oven, underglaze decoration requires great skill, especially where the effects of light and shade are desired.

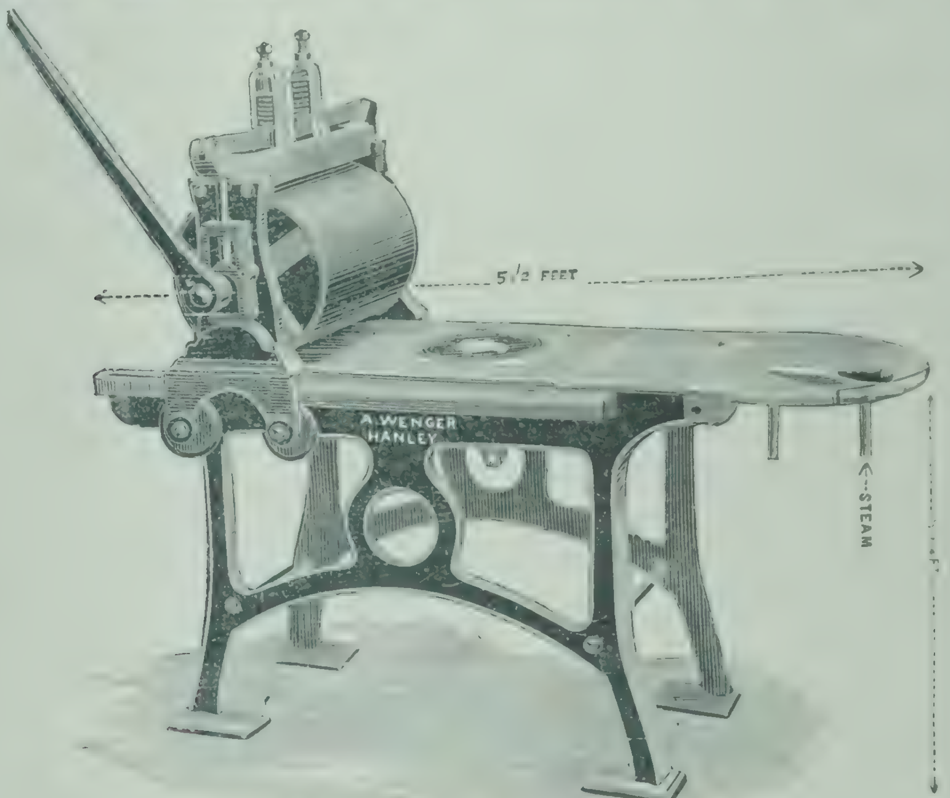


FIG. 19.—Printing Table.
(*By courtesy of Messrs Wengers Ltd.*)

The decorated ware is next heated to a dull redness in a hardening chamber or kiln so as to burn off the turpentine and any other organic matter present, after which it is dipped in glaze, and then sent to the glost oven.

In overglaze decoration the same methods are employed, but they are applied to the glazed ware instead of to the biscuit. Owing to the wide range of colours required, these are seldom heated to more than 900° C. The colours are finely ground, and then mixed with a flux such as :—

Red lead	3 parts.
Borax	2 ,,
Flint	1 part.

This flux is really a readily fusible glaze, and its purpose is to fix the colour to the ware so as to cover and protect it, and to give a glossy finish where this is required.

The painting of overglaze work is easier than that of underglaze as the colours change but slightly in the oven, and losses in firing are very small. It is specially used for heraldic ware, gilding, and for many classes of pottery bearing elaborate chromo-lithographic designs.

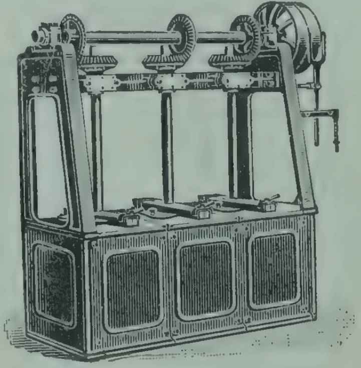


FIG. 20.—Colour Mill.

(By courtesy of Messrs T. Willett & Co.)

TUNNEL KILNS

Overglaze decorated ware is usually fired in **muffles**, but several firms who have used a simple form of **tunnel kiln** (Fig. 16) have found it more economical and satisfactory. In this kiln the goods are placed in iron baskets or on small cars at one end of the tunnel, and are moved forward until they reach the centre. This is the hottest part of the kiln, and as soon as the ware is "finished" it is moved forward towards the other end of the kiln. The temperature of the ware then falls gradually, and on removing it from the kiln it can be handled without inconvenience.

The heating is effected in such a kiln in a remarkably uniform and economical manner, and the gradual rise and fall in the temperature of the ware is conducive to satisfactory results coupled with a large output. Such kilns are better than the ones formerly used for this class of work, but they require a large output if they are to be worked economically. Modern tunnel kilns for firing on-glaze decoration are almost universally heated electrically owing to the simple, automatic regulation, the clean atmosphere obtainable, and the reduction in loss at this, the final stage in manufacture involving a firing process. For the small firm or studio potter an interesting recent development is the intermittent, electrically-heated, chamber oven which is a "half-way house" between the traditional intermittent enamel kiln and a tunnel kiln.

For the larger manufacturer, gas (town or producer) seems to be preferred for biscuit and glost, although a number of electric kilns for both are now in existence and working satisfactorily. In the Potteries district of Britain the town gas supplied for consumption in the ceramic industry in 1949 amounted to 3,660,844,700 cu. ft.

Tunnel ovens of different construction vary considerably in efficiency and it is doubtful if the last word in tunnel oven design has yet been said. Performance figures for three types of tunnel kilns firing biscuit tiles are shown in the table below.

For further particulars on overglaze decoration see the section on **Porcelain** (p. 195).

PERFORMANCE FIGURES OF THREE TUNNEL OVENS FIRING BISCUIT TILES

Type.	(*a*) Open flame, large section.	(*b*) Open flame, small section.	(*c*) Muffle, section as (*b*).
Length - - - - -	400′	426′	400′
Section - - - - -	5′ 3″ × 4′	3′ 5″ × 3′ 4″	3′ 5″ × 3′ 4″
Temperature - - - -	1,160° C.	1,280° C.	1,280° C.
Firing cycle - - - -	137 h.	90 h.	98 h.
Throughput/24 h. - - -	16.57 tons	30.4 tons	25.6 tons
Fuel: producer gas from - -	Anthracite	Brown coal briquettes	Bit. coal
Calorific value of solid fuel B.Th./lb. - - - -	13,600	8,640	12,600
Consumption - - - -	8.57 tons	9.10 tons	8.0 tons
Heat units per lb. ware (including producer losses) - - -	5,940	2,124	3,139

Illustrations of modern tunnel kilns are shown in Figs. 21 and 22.

Fig. 21 shows an electrically heated, circular kiln for decorated ware (Gibbons, Wild Barfield), whilst Fig. 22 shows a typical gas-fired kiln for glost earthenware table-ware and the method of packing the ware (Gibbons).

The fuel economies and time saving to be derived from the use of tunnel kilns instead of the old-fashioned intermittent oven may be seen from the following comparative table adapted from Rosenthal, "Pottery and Ceramics," following Gatzke (*Ber. d. D. Ker. Ges.*, 1936).

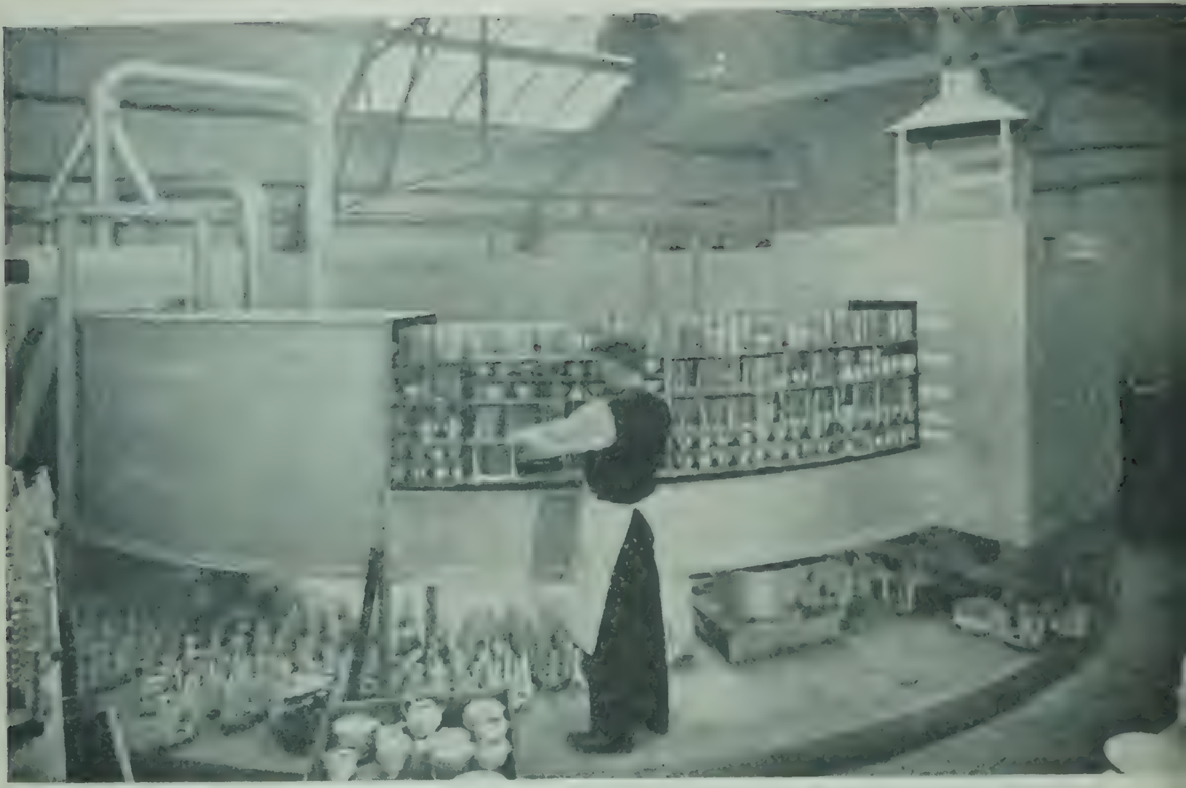


FIG. 21.—Circular Decorating Kiln, electrically heated.
(Courtesy Gibbons-Wild, Barfield.)

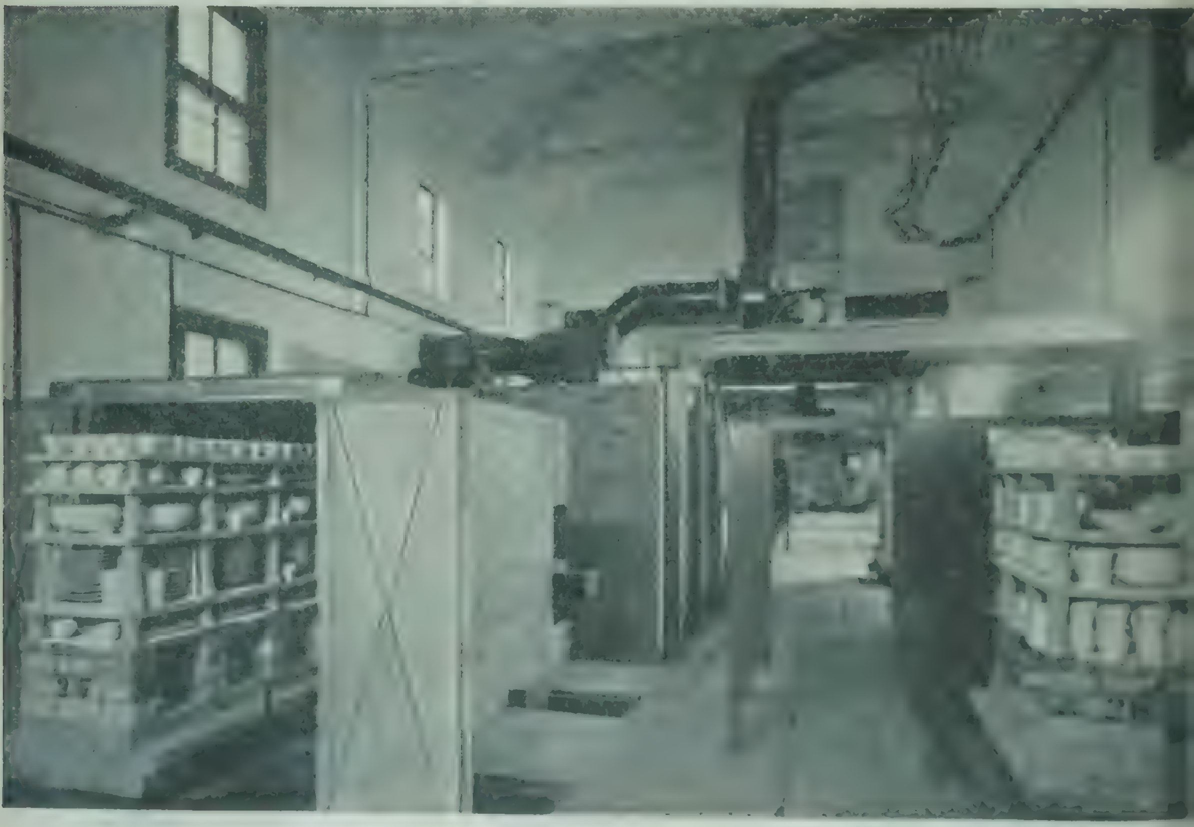


FIG. 22.—Muffled Kiln, Glost Earthenware.
(Courtesy Gibbons-Wild, Barfield.)

Apart from the saving in time and in the cost of fuel and kiln furniture, other advantages of tunnel kilns compared with intermittent ovens are the much less exacting demands they place on the physique of the factory personnel, particularly in respect of loading and unloading, and the much better general working conditions: the product is more uniform and the rejects lower.

Ware fired.	Peak Temp. of Firing °C.	Intermittent Ovens.		Tunnel Ovens.		
		Firing cycle* hrs.	Lb. fuel per lb. ware.	Firing cycle hrs.	Lb. fuel† per lb. ware.	kWh.‡ per lb. ware.
Porcelain table-ware	1,410	76	$3\frac{1}{4}$–4	28–40	$1\frac{1}{2}$–$1\frac{3}{4}$	$1\frac{1}{8}$–2
Earthenware, biscuit	1,280	72	1	27–37	$\frac{1}{4}$	$\frac{1}{2}$–$\frac{2}{3}$
,, glost	1,150	72	1–$1\frac{3}{4}$	17–30	$\frac{1}{3}$	$\frac{1}{2}$–$\frac{2}{3}$
San. Earth, biscuit	1,280	86	$1\frac{1}{4}$–$1\frac{1}{2}$	38–48	$\frac{1}{2}$–$\frac{2}{3}$	$\frac{3}{4}$–$\frac{4}{5}$
,, ,, glost	1,150	76	$1\frac{1}{2}$–2	32–40	$\frac{1}{2}$–$\frac{2}{3}$	$\frac{2}{3}$–$\frac{3}{4}$
Wall tiles, biscuit	1,280	180	$\frac{1}{2}$–$\frac{2}{3}$	80–100	$\frac{1}{7}$–$\frac{1}{4}$	$\frac{1}{4}$–$\frac{3}{8}$
,, ,, glost	1,060	160	$\frac{2}{5}$–$\frac{1}{2}$	30–50	$\frac{1}{5}$–$\frac{1}{3}$	$\frac{1}{5}$–$\frac{3}{10}$
Floor tiles	1,280	230	$\frac{3}{10}$–$\frac{2}{5}$	100–120	$\frac{3}{10}$–$\frac{2}{5}$	$\frac{1}{4}$–$\frac{3}{8}$

* Does not include the time required to empty and refill the oven; this lost time, amounting to several days per oven, falls away completely in the tunnel oven as the loading and unloading of the trucks does not interfere in any way with the passage of goods through the oven.

† Includes producer losses. ‡ Electric tunnel oven.

Probable future progress.—Mass production involves large units operating standardised processes under automatic or instrumental control with the widest possible elimination of the human factor; *i.e.*, the opposite pole to the methods of the craftsman. The battle of continuous versus intermittent firing, which largely occupied the attention of the passing generation, now seems to have been decisively won and the next battle to be engaged will be that of elimination of unnecessary operations or processes and the utmost possible mechanisation of those which remain. Automatic making machines are knocking at the door and it seems practically certain that they will soon push it wide open, wherever industry is alive to the challenge of the changing world. It is difficult to avoid the conclusion that there will be a certain number of still larger units than those already engaged in the industry or, alternatively, a much more extensive standardisation of raw materials and processes, so that a number of separate producing units will be in a position to manufacture more or less identical and, therefore, interchangeable wares. For instance, one unit might manufacture nothing but flat ware, while another made nothing but hollow. The introduction of tunnel ovens makes it possible to standardise completely the firing, which is possibly the most important single process in pottery manufacture, but two ovens firing on the same schedule cannot deliver similar products unless the ware which enters the ovens is similar and responds in the same way to the firing treatment. The potter, at present, has very little control over his raw materials and the responsibility for ensuring uniformity lies on the supplier, whose specification is usually little more than "as previously supplied." Much more extensive blending of raw materials, and a reduction in the number of varieties demanded, appears to be an inescapable consequence of, and prerequisite for, increased standardisation of the manufacturing processes.

One of the most interesting recent developments is the fully automatic making machine, which has been introduced successfully at several stages of manufacture in various branches of the industry, *viz.*, dust-pressed tiles, electrical porcelain, and domestic earthenware and porcelain. There is little doubt that this process will continue under the stress of competition, particularly among the mass-production factories, with the result that control by craftsmen will gradually give way to control by engineers and technicians in most of the manufacturing processes.

SECTION LXVII

PORCELAIN

BY ALFRED B. SEARLE
REVISED BY MARCUS FRANCIS

LITERATURE

In addition to works mentioned on p. 161, the following more specialised books may be consulted:—

H. HEGEMANN.—"Die Herstellung des Porzellans." 1938.
R. RIEKE.—"Das Porzellan." 1928.
M. LARCHEVÈQUE.—"Fabrication industrielle des porcelaines." J. Baillière, ed., Paris, 1928.
E. GRAMS.—"Das Porzellan." Sprechsaal, Coburg, 1951.

PORCELAIN is the noblest kind of pottery, its distinguishing feature being the possession of a vitrified, impervious, and translucent (or semi-transparent) body. There are many varieties of porcelain, some of them differing very widely from the others, the chief ones being (*a*) hard porcelain, (*b*) soft or tender porcelain, (*c*) china or bone porcelain, and (*d*) Parian ware—a variety of unglazed porcelain used for statuary, etc.

The general characteristics of the various porcelains have been briefly described under **Pottery** (p. 161).

Raw Materials.—*China clay or kaolin* is one of the chief constituents of porcelain, and the quality of the ware will vary according to the particular clay or kaolin used, the amount of flux and the firing.

Deposits of kaolin occur in various parts of Europe, the most famous being near Karlsbad, Meissen, Germany, Czechoslovakia, St Yriux near Limoges, France, and the Cornish china clays in England. The German kaolins are largely derived from porphyry though some are of granitic origin. The French kaolins are derived from a species of gneiss (pegmatite), and the Cornish china clays have been formed by the decomposition of granite. Chinese and Japanese porcelains have been famous for many centuries.

Kaolins are white soft earths which differ from each other slightly in composition and texture, and even more so as regards the porcelain produced from them, but their characteristics are sufficiently marked for them to form a distinct variety of clay. When washed free from the coarser impurities, kaolin and china clay consists chiefly of an aluminosilicic acid, $H_4Al_2Si_2O_9$, the crystalline form of which occurs as the mineral kaolinite. In most kaolins the particles are so minute that it is almost impossible to ascertain whether they are crystalline or amorphous, and the length of time they remain in suspension in water has led to the conclusion that they are partly colloidal in nature.

Most kaolins are almost devoid of plasticity, but this property differs greatly in those of various origins. This lack of plasticity distinguishes the kaolins from the plastic clays and necessitates the employment of somewhat different methods of manufacture.

The chief impurities in kaolins and china clays are quartz, felspar, mica and various igneous rocks, some of which contain iron compounds. These may be largely removed by washing or elutriation, but even the refined product contains upwards of 10 per cent. of impurities. Some of the kaolins used by the Chinese contained 25-30 per cent. of mica.

Felspar—chiefly from Norway—is a typical constituent of porcelain, in which it forms the chief flux and thereby gives translucency to the ware. It is a hard rocky material composed of 64.8 per cent. silica, 18.3 per cent. alumina, and 16.9 per cent. potash or an equivalent base such as soda or lime (see p. 171).

There is a considerable variety of felspars of similar characteristics but different compositions. The figures just mentioned refer to the variety known as orthoclase, which is the one chiefly used in pottery manufacture, though plagioclase felspars are also used to a small extent.

Cornish stone or china stone is a felspathic material occurring in Cornwall and used in the manufacture of English china and of some glazes. It is supposed to be similar to the Chinese *Pe-tun-tse* and to the French *pegmatite*, but differs from them very considerably in several important respects, and especially in fusibility.

The varieties of Cornish stone chiefly used have a composition corresponding to 6 per cent. potash, 18 per cent. alumina, and 76 per cent. silica and may be regarded as a mixture of felspar and quartz, though artificial mixtures of these two minerals do not produce quite the same results.

Quartz in the form of white sand, powdered quartz, or ground flint is used to reduce shrinkage in the ware and to provide the requisite amount of free silica (p. 173).

Steatite—a complex magnesium silicate—is used in the production of some porcelain such as insulators. It acts as a flux and also increases the plasticity to a small extent.

Chalk or some other form of calcium carbonate is largely used in the manufacture of hard or true porcelains. It has a powerful influence in effecting the fusion or vitrification of the body (see p. 172).

Magnesite, or magnesium carbonate, is occasionally used as a partial substitute for chalk.

Grog, or ground biscuit ware, is conveniently used in some porcelain glazes. It is also convenient for introducing clays into a body without altering the plasticity and moisture of the other materials. It consists simply of clean pieces of unglazed ware which have been crushed to powder (see p. 173).

Bone ash is prepared by heating the cleaned bones of oxen until a white mass is obtained which is then ground to powder. It consists chiefly of calcium phosphate with a little calcium carbonate and fluoride, and is a powerful flux.

As a constituent of porcelain it gives to the paste a plasticity fully as great as that of hard porcelain combined with the same range of colours as are available for the glassy porcelains.

Porcelain Bodies.—As stated on p. 163, there are many varieties of porcelain, and their compositions vary correspondingly. It is therefore necessary to consider each type of porcelain separately.

Hard porcelain is made with a body composed chiefly of kaolin, felspar and quartz, the proportions of each being adjusted to produce the desired effect.

Typical mixtures consist of—

	Sèvres.	Berlin.	Chinese.
Kaolin - -	38	77	47
Felspar - -	38	23	15
Quartz - -	24	...	38

The large proportion of clay and the absence of quartz in the figures given for Berlin porcelain are due to the fact that the Senewitz kaolin used there is so rich in mica. This mixture really corresponds to a porcelain made of clay substance 53 per cent., felspar 23 per cent., and quartz 22 per cent. From this it will be seen that the proportions of felspar and quartz used depend on the proportion of clay substance in the kaolin. The less quartz and felspar the harder will the porcelain be to burn, but the more resistant will it be to changes in temperature. For chemical ware more clay is used. For very large articles, ground biscuit porcelain may be added so as to reduce the shrinkage without altering the composition. If the proportion of the last-mentioned material is large it may be necessary to add a little plastic clay to bind the particles together.

For electrical purposes (insulators, etc.), hard porcelain is extensively used. For this purpose, it must be fired at the highest temperature possible, and the ware must be rich in sillimanite or similar crystals. Owing to the demand for specially efficient insulators, the best of these are now made exclusively of china clay or of steatite, and, in the case of Marquardt porcelain, of china clay to which alumina has been added to make it more refractory.

Porcelain used for electrical and some other engineering purposes must be made with special care, and screws and other fittings must be almost as accurate as if made in metal.

The *glazes* used for hard porcelains are composed of the same ingredients as the body, but in different proportions, and chalk or marble is sometimes added so as to obtain a more fusible product.

A typical glaze for hard porcelain is that of Sèvres, which is made of—

Ground hard porcelain (grog)	25 parts,
Quartz	42 ,,
Chalk or marble	33 ,,

or that of the Royal Berlin Works, which is made of—

Felspar	8 parts.	Quartz	57 parts.
Kaolin	28 ,,	Marble	7 ,,

Glassy porcelains are nowadays of little or no industrial importance.

Those made in France were composed of a calcareous clay or marl with a large proportion of fusible material, and closely resemble glasses of a complex character. In some cases so little clay was used that dextrin had to be mixed with the body to give it the necessary cohesion. The famous *pâte tendre* of Sèvres was made by fritting (p. 162) together—

Sand	60.0 parts,	Alum	3.6 parts,
Nitre	21.8 ,,	Gypsum	3.7 ,,
Salt	7.2 ,,	Soda	3.7 ,,

and mixing the frit thus formed with chalk and Argenteuil marl in the following proportions:—

Frit	75 parts.
Chalk	17 ,,
Marl	8 ,,

The composition of this porcelain closely resembles that of plate glass.

The *glazes* used for glassy porcelains are much more fusible than those for hard porcelains, and resemble the glazes used for earthenware. For French or glassy porcelain a typical glaze may be made by fusing together—

Litharge	38 parts,	Potash	15 parts,
Fontainebleau sand	27 ,,	Soda	9 ,,
Flint	11 ,,		

grinding the product and mixing it with water to form a slip.

For **bone china** or **English china**, the body is now composed of—

China clay	20–30 per cent.
Bone ash	27–46 ,,
China stone	20–32 ,,

Wide variations occur in china obtained from different works, particularly with regard to the proportion of bone ash and china stone. A little ball clay is also added by some potters in order to increase the plasticity of the material.

Some of the earliest English chinaware bore a close resemblance to French porcelain, and it was only when Spode, about the year 1800, abandoned the use of glass that true English china was manufactured.

At one time or another almost every variety of porcelain has been manufactured in England, but what must be regarded as true English chinaware is made, as stated above, of china clay, Cornish stone and bone ash.

A typical glaze for such English or bone china is made of—

FRIT.	
China clay	12 parts.
Quartz or flint	15 ,,
Cornish stone	20 ,,
Chalk or whiting	18 ,,
Borax	35 ,,

GLAZE.	
Frit	65 parts.
Cornish stone	11 ,,
Flint	11 ,,
White lead	13 ,,

From this it will be observed that the glaze on English chinaware bears a very close resemblance to that used for the finest English earthenware. It differs less from the composition of the body, but the presence of lead, borax, and whiting have so great an influence that it is difficult to find any resemblance between the composition of the French and English glazes, and those used on the hard porcelains of the Continent and the East.

It is, in fact, largely owing to this difference in the composition and behaviour of the glaze that English and French porcelains possess so few of those special characteristics which render hard porcelains so valuable both æsthetically and for scientific and other purposes. The glaze on a hard porcelain so closely resembles the more fusible portions of the body to which it is attached that it has been aptly compared by W. Burton to the skin of the human body; the same writer comparing the glaze of French and English porcelain to a tight-fitting garment of an entirely different composition from the body which it clothes, or to a varnish covering applied to an article.

Parian ware is an unglazed porcelain which is admirably suited to the production of statuary. It has, however, also been glazed with a mixture similar to that used for earthenware or bone china, and then used with great success in the manufacture of table ware and vases. **Beleek porcelain**—the only porcelain made on a commercial scale in Ireland—is a glazed Parian ware.

According to W. Burton, glazed Parian ware corresponds exactly to the so-called Chinese soft paste porcelain, for which fabulous prices were at one time paid.

Parian body should be made of the same material as true porcelain, though the proportion of felspathic material is much higher.

A widely used recipe recommends—China clay, 1 part; felspar, 2 parts.

This is much more fusible than true hard paste porcelain. Some makers use the foregoing with an equal weight of white sand, and other potters have used glass and other fluxes in the manufacture of Parian ware. In one firm, the Parian body consisted of equal weights of hard paste and glaze. Great care is, however, required in the use of fluxes, or the ware will have an unpleasant greasy appearance, due to the excessive vitrification.

Like other porcelains, Parian body has so little plasticity that it is difficult to manipulate, and the best results are most readily obtained by casting (p. 182).

The shape of the articles must be within certain limits; some projections may be supported by pieces of raw body in the kiln, but this is always difficult in the case of the extended legs of prancing horses and of other figures with projecting parts.

Chinese and Japanese porcelain wares are frequently made of naturally occurring mixtures. Thus the Japanese Imari ware is made of a material containing 49 per cent. clay substance, 14 per cent. quartz and 37 per cent. felspar.

The ancient Chinese were, however, well acquainted with the use of felspathic material as a means of adjusting the composition of their raw material, and termed the latter *Kao-lin* and the former *pe-tun-tse*. The best examples of Chinese porcelain are of the hard paste or true porcelain type already described.

PROCESSES OF MANUFACTURE

Preparation of Porcelain Bodies.—The mixing of the various ingredients composing the porcelain bodies is effected in a manner very similar to that used in earthenware (p. 176), and consists essentially in reducing the various materials into the state of a fine powder, suspending them in water in the form of a slip or cream, mixing the various slips thoroughly together in the desired proportions, and then removing the surplus water by means of a filter press.

On the Continent the filter cakes are stored in cool cellars for much longer periods than is usual in this country, this storage being intended to develop as much plasticity as possible. When the cakes are ready for use they are passed through a kneading machine or mixer. Magnets for removing adventitious particles of iron from the slip are also employed (p. 178).

It is necessary that the material used for the manufacture of each kind of porcelain should be mixed in the requisite proportions and with the necessary thoroughness, as, otherwise, the shrinkage in drying and burning will be excessive or irregular, and the ware will not have the properties characteristic of good porcelain.

The methods of producing articles from porcelain paste vary considerably in different countries, but they are usually modifications of those previously described in connection with earthenware (p. 179), and comprise **moulding** or pressing by hand in plaster moulds, **throwing** or shaping on a potter's wheel, and **casting** or pouring a slip into a porous mould.

As porcelain bodies are usually deficient in plasticity, and the demand for thin, translucent pieces is very large, they are difficult to throw or mould, so that casting is the most suitable process where a sufficient number of articles is required. Additional parts, such as handles, are attached in the same way as to earthenware (p. 172). The bodies used in the production of French or glassy porcelain are exceptionally difficult to shape on account of their lack of plasticity, and this, coupled with the hazard and uncertainty of the effects of heating in the oven or kiln, has prevented this class of porcelain from becoming commercially profitable.

In order to obtain very thin ware without casting, the ancient Chinese were compelled to throw the vessels much thicker than was required, and subsequently to scrape them down to the required thinness.

Variations in minor details naturally occur in different works and at different periods, but these are beyond the scope of the present book. There is a general inclination to use labour-saving machinery, and to limit the number of shapes made.

When a porcelain vessel has been produced by any of the foregoing methods it may be decorated by modelling or carving as desired, and any inaccuracies in shape may be remedied.

It is precisely at this stage of the manufacture that the individuality of the potter is revealed, though under the conditions prevalent in many modern factories much individuality is prohibited.

The ware is next allowed to dry slowly, without cracking or warping, after which it is sent to the biscuit oven to be fired for the first time.

The object of the first firing is to harden the body of the ware and to facilitate the application of the glaze. This is accomplished, in the case of the Japanese, French, and German **hard porcelains**, at a temperature of 600°-700° C.; the Copenhagen porcelain is first fired at 950° C.

It is not intended to produce any other effect than those mentioned, as the best porcelains are those in which the changes effected by heat in both body and glaze occur simultaneously, the final temperature, which is between 1,200° C. and 1,500° C.,[1] having similar influence on both body and glaze. The Chinese have long been well aware of this fact, and most of their porcelain is glazed previous to its being fired, though some colours obtained by them could only have been produced by firing the unglazed ware (biscuit) to a very high temperature, and then using a more readily fusible glaze.

The **glassy porcelains** are fired to a temperature of 1,100°-1,150° C. before glazing, and English **chinaware** (bone china) to about 1,250° C., but in both these classes of porcelain the glaze is fired at a lower temperature than the unglazed body—usually below 1,100° C.

In other words, the properties of the body in glassy porcelain, bone china, and glazed Parian ware are completely developed in the first firing, and the glaze forms an outer covering of an entirely different nature.

The temperature of the kiln or oven must be raised very slowly and cautiously at first—even more so than for earthenware (p. 187). At 500°-600° C., when the clay begins to decompose, the heating must also be very cautiously managed, after a temperature of 850° C. has been reached, however, the rise may be more rapid. As the finishing temperature is approached the greatest possible care is required, as a slightly excessive temperature will cause a large quantity of the ware to collapse from over-heating. To obtain the best results, the ware must be maintained at an almost constant temperature for some time towards the close of the firing.

If the ware is to be decorated "underglaze" it is taken, after the first firing, to the decorators: otherwise it is ready for glazing. For information on decorating see p. 200.

---

[1] See footnote on p. 200.

The firing atmosphere should usually be reducing, so as to prevent the discoloration of the ware by any iron compounds which may be present.

The burned ware is sorted carefully, the proportion of damaged and useless material being large, except in the most carefully managed works.

On burning, the felspathic material melts first, and the molten portion then attacks the other constituents, forming less fusible substances. As the temperature rises, more fusion occurs and a point would, in time, be reached at which there would be so much fused material that the articles would begin to collapse. Firing is stopped just before this stage is reached, so that thin sections of hard porcelain, when viewed under a microscope, are seen to consist of particles of calcined clay united together by means of a glassy substance. Minute needle-shaped crystals of sillimanite ($Al_2O_3SiO_2$) are formed at a temperature of about 1,200° C., and are a characteristic constituent of hard porcelains.

The application of the glaze to porcelain is usually effected by dipping the once-fired article in a suitable slip or slurry, as in the glazing of earthenware (p. 187).

The Chinese preferred sprinkling the body with the glaze-slip, and obtained some of their finest effects in this manner, though with infinite labour and unparalleled dexterity and skill. A modification of the Chinese method of spraying is now used in Europe for producing certain colour effects, a special form of aerograph being employed for this purpose.

Where dipping is impracticable the glaze is painted on with a brush, some eight or ten coats being usually needed. As each coat must be allowed to dry before the next is applied this operation occupies a considerable time, and does not yield so even a coating as that on articles which have been dipped.

A perfect glaze adheres tightly and uniformly to the body; it has the same coefficient of expansion as the body, and shows no bare cracks or flakes. The glaze must not fuse too readily, or it will collect in drops instead of being uniformly distributed. The necessary conditions are best fulfilled when the glaze is not too low in alumina, as glazes which are free from alumina adhere badly to porcelain.

The glaze must be glossy, it must be completely fused whilst in the kiln, or when cooled must be transparent, free from bubbles and spots, and so hard that it is not scratched by steel. Porcelain owes most of its beauty, gloss, and cleanliness in use to its glaze, and to the great similarity between the glaze and the body. These characteristics can only be obtained in the most complete manner by the use of specially selected materials, and by firing both body and glaze at a much higher temperature than is used for earthenware.

When the coating of glaze is quite dry it is carefully rubbed, so as to remove any inequalities, and the ware taken to the placers, who fix it carefully and skilfully in saggers (p. 187) by means of suitable supports, so that none of the glaze is removed and the glazed parts are kept as free as possible from contact with other surfaces. The saggers, after being filled, are piled one above another in the oven.

The temperature to which the glaze must be fired depends, as already explained, on the nature of the porcelain. For hard porcelains it is the same as that of the body—about 1,200°-1,500° C.—but for chinaware and French porcelain it is much lower—about 1,050°-1,100° C.[1]

The time required for firing in the glost kiln is naturally much less than if the ware had not been previously heated. Even with the hardest porcelains it seldom exceeds forty hours, and a much shorter time is usually sufficient.[2]

Decoration.—The colours used in the decoration of porcelain are similar to those used for earthenware (p. 187), but for underglaze porcelain the range of colours is severely limited by the high temperature at which the ware is fired.

The best **underglaze** colours used for porcelain are cobalt oxide for blues, chromium oxide for greens, uranium oxide for black and yellows, copper for red, and platinum, vanadium, and titanium for other colours. These various oxides are applied in the form of a thick fluid made by mixing them with turpentine, or they may be added to the glaze in the proportion of 2-5 per cent. of the latter.

---

[1] The reason for the great variation in the finishing temperature stated for hard porcelain is to be found in the composition of these materials. For most hard paste porcelains the temperature in the glost oven does not exceed 1,250° C., but several Continental works insist that they invariably finish at Seger cone 18 (1,500° C.).

[2] The kilns or ovens used are similar to those described for burning earthenware (p. 186), though small variations in the efforts made to enable the higher temperature to be more readily reached are the cause of the ovens in different works being distinct in several important details. These are, however, matters for the manufacturer and expert rather than for those for whom the present volume is intended.

If the oxide is precipitated along with alumina, and the product thus obtained is used as a colour, the tints produced are entirely different from those obtained by the direct use of the oxide.

It is not usual to add colouring metallic compounds in the form of a *solution*, though there are some advantages in this form. Solutions of cobalt chloride or nitrate in water are occasionally employed; they are added to the glaze or to the body, but are of greater value in neutralising an undesirable yellow tint than as direct pigments. In underglaze colours it is difficult to get graduated tints, as the biscuit absorbs the colour so rapidly.

This may largely be overcome by the use of aerographs (described on p. 200).

The **overglaze** or muffle colours used on porcelain can be fired at temperatures to suit the tint required, and as they are quite independent of the ware a very wide range of colours is possible. These overglaze colours are usually prepared by fusing the colouring metallic oxide with a flux, such as a mixture of 6 parts of red lead, 2 parts of quartz, and 1 part of borax. The fused mass is ground to a fine powder, mixed with fat, oil of turpentine, and then painted on the glazed porcelain.

The chief colouring oxides are similar to those used for earthenware, and include:—

Blue overglaze—1 part cobalt oxide, 2 parts zinc carbonate, and 5 parts of flux. Other cobalt mixtures are also used.

Green overglaze—chromium or copper oxide.

Yellow overglaze—lead antimoniate, titanium oxide, uranium oxide.

Red overglaze—iron oxide or hydroxide prepared in various ways.

Carmine overglaze—purple of Cassius, *i.e.*, metallic gold precipitated on tin oxide or alumina.

Pink overglaze—chromium oxide precipitated on tin oxide or alumina.

Dark brown overglaze—manganese oxide.

Black overglaze—uranium oxide or metallic iridium.

White overglaze—tin oxide.

Silver overglaze—a mixture of gold and platinum. Metallic silver cannot be used.

Gold (as in *gilding*) may be produced by two methods: (*a*) A mixture of powdered metallic gold, bismuth oxide, and oil is rubbed into a thin paste, and is applied to the ware with a brush. After burning, the gold is dull, but becomes glossy if rubbed with a burnishing tool. (*b*) A cheaper method consists in preparing a 15 per cent. solution of gold in a sulphurous oil (gold balsam). This material produces a bright gold when burned, and therefore requires no burnishing.

The burning of overglaze colours is effected in muffle ovens or small tunnel kilns (p. 191). The goods are carefully watched, and the heating is stopped or the goods are removed as soon as the glaze is sufficiently fused.

Excessive fusion must be avoided or the colours will run into each other. The temperature reached is between 800° and 1,000° C., but must be suited to the particular colours in the oven. Where several colours requiring different temperatures are used in the same piece of ware, it will be necessary to apply colours one at a time in the order of their ability to resist high temperatures, the most refractory being applied first. Some pieces of ware must be fired six or more times.

Crackled ware is a variety of porcelain in which the surface of the glaze is traversed by innumerable small hair-like cracks. This is due to the glaze having a coefficient of expansion higher than that of the body; ordinarily it is regarded as a defect and is then termed *crazing*, but when effected purposely—as in Chinese crackle ware—it is usually produced by means of a calcareous slip applied between the body and the glaze, or by replacing some of the lime in the glaze by an alkali and reducing the proportion of alumina.

Crystalline glazes, known to the ancient Japanese, were first introduced into Europe (at Sèvres) in 1850. Since then they have become increasingly popular, especially those in which the surface of the ware is so completely covered with minute crystals as to present a *matt* appearance. Larger isolated crystals are more difficult to control, but sometimes produce very beautiful effects.

The crystals are due to the glaze being supersaturated with one or more oxides which form readily crystallisable silicates—zinc and titanium oxides being the most used. Molybdenum, tungsten, vanadium, uranium, copper, manganese, and chromium compounds also assist in the production of crystals if the glaze is, otherwise, suitable. The coating of glaze must be rather thicker than usual, and it is not unusual to apply a highly siliceous glaze containing the special oxide after the ware has been covered with the ordinary glaze. If colouring oxides are present their crystals sometimes exercise a selective action, and produce very beautiful colour effects.

Matt glazes may also be produced by adding a body to the glaze—equal volumes of each being frequently used.

Flowing glazes consist of one or more coloured glazes which are applied to the unfired surface of other glazes of a slightly less fusible nature. On firing, the uppermost glaze sinks partially into and flows partly over the underglaze, and produces characteristic and beautiful blendings of colour.

The best results are obtained with a copper or manganese glaze on a black background, or with a cobalt oxide glaze on a yellow or red glaze.

The term "flowing glaze" is also applied to the effect produced by chloride of lime placed near to the glazed surface in the oven. Volatilisation occurs and a "blush" effect is produced. As the result is difficult to control it is better to produce the same effect by spraying the colour on to the ware.

Rouge flambé is a bright red glaze produced by the action of reducing gases on a glaze containing copper oxide.

It was known to the ancient Chinese, but its production on hard European porcelains is a relatively recent discovery.

Lustre glazes are characterised by the beautiful sheen and iridescence which they exhibit. These effects are largely due to momentary changes in the atmosphere of the kiln.

At one time, potters depended almost entirely on accidental variations in the firing to produce lustrous glazes, but it is now possible to make them in a reasonably reliable manner. The work is one requiring exceptional skill, as the metallic films producing the lustre are extremely thin, and it is very difficult to get them reduced so as to give a pleasing effect. Some firms have been particularly successful with this kind of ware.

ELECTRICAL PORCELAIN

LITERATURE

The following deal more particularly with ceramic bodies for electrical purposes:—

- E. Albers-Schönberg.—"Keramische Hochfrequenz-Isolierstoffe." 1939.
- E. Schwandt.—"Keramische Baustoffe für die Hochfrequenztechnik." 1933.
- G. Beneschke.—"Die Porzellan-Isolatoren." 1923.
- W. Demuth.—"Die festen Isolierstoffe der Elektrotechnik." Schloss Bleckede Elbe. 1951.
- B.I.O.S. Reports, 1429, 1459. H.M.S.O., 1947–8.
- R. Russell, Jr.—"Electrical and Technical Ceramic Industry of Germany." Brooklyn, 1947.

Electrical Porcelains.—Low-tension electrical porcelain fittings are composed of a body which is little more than a hard-fired earthenware body. On the other hand, electrical porcelain for high-tension work must have a much greater electrical and mechanical strength and is very much akin to a true hard-paste porcelain. The optimum qualities appear to be developed when the composition and firing conditions are such as to produce an interlocking network of mullite crystals in a glassy matrix.

Steatite Bodies.—If high frequencies are also involved then electric porcelains of improved electrical properties—in particular, low dielectric loss—must be employed. Initially these were based on steatite, a mineral composed almost entirely of crypto-crystalline talc ($H_2Mg_3Si_4O_{12}$), together with small additions of clay to improve its working properties and small amounts of felspar or other fluxes to enable it to be fired to a dense mass at the temperatures employed (ca. 1,400° C.). These bodies are sometimes referred to as *clino-enstatite* bodies, because a crystalline substance known as clino-enstatite ($MgSiO_3$) forms in them during firing: this is held responsible for the low power loss of these bodies. They are also mechanically stronger than straightforward porcelains. If magnesium oxide or carbonate is added the electrical properties are still further improved but the thermal expansion also increases, which may be a disadvantage for certain purposes. The improved electrical properties are ascribed to the formation of *forsterite* (Mg_2SiO_4).

Cordierite Bodies.—If sufficient clay be added to steatite the maturing temperature of the body, *i.e.*, that firing temperature which must be attained (and possibly maintained) in order to produce the desired characteristics in the finished material, is lowered. The product has a remarkably low coefficient of expansion combined with high mechanical strength, which gives it excellent thermal shock resistance. This is due to the formation of *cordierite* ($Mg_2Al_4Si_5O_{18}$). The electrical properties are no better than that of true porcelains.

Condenser Bodies.—With the development of radio there has arisen a demand for bodies of high dielectric constant combined with a reasonably good power factor. The starting point for most of these is titanium dioxide which, in the form of rutile, has a dielectric constant of about 100 at 10 megacycles, compared with a figure of 6 for clino-enstatite bodies at the same frequency. The addition of zirconium dioxide removes certain disadvantages of these bodies at some loss of dielectric strength. Mixtures of titanates of the alkaline earths with other additions are capable of yielding bodies with dielectric constants of the order of many thousands, but they are too temperature-sensitive for general use. The highest practical value appears to lie in the neighbourhood of 1,000 and is reasonably constant over a range of temperatures from −15 to +60° C. The power factor over this temperature varies from about 2.1 per cent. at the lower end to a minimum value of 1.46 per cent. at about +30° C. and 1.56 per cent. at 60° C. Bodies based on barium titanate are now available with dielectric constants which change but little over the range −30° C. to +130° C.

Zircon Porcelains.—The incorporation of zircon in suitable ceramic bodies has been found to result in increased mechanical strength and good thermal shock resistance, together with favourable electrical properties.

Spark Plug Bodies.—The earlier porcelain spark plugs for internal combustion engines soon gave way to plugs made from steatite (clino-enstatite bodies), owing to the greater mechanical strength and higher electrical resistance of the latter at elevated temperatures. Increasingly exacting working conditions have finally led to the development of plugs made of practically pure aluminium oxide sintered to a dense mass at firing temperatures in the neighbourhood of 1,800° C. (See Table below).

A spark plug body may be regarded as a special type of electrical porcelain; namely, one for high temperature use.

Performance Figures for Some Ovens for Firing Spark Plugs.

Type.	Length in ft.	Firing Cycle in hrs.	Temp. °C.	Fuel.	Consumption per 1,000 plugs in cu. ft.
Round oven	...	36	1,630	Town gas, C 450 B.Th.U. per cu. ft.	6,000
McDougal rapid oven	53	2	1,630	,,	1,910
Dettmer tunnel oven	59	8–10	1,630	,,	1,560
Dettmer tunnel oven (Wistra)	26	10	1,630	,,	1,275
Kera-tunnel,					
type ZK III	55	24	1,630	,,	940
type ZK 5	85	24	1,630	,,	900
type ZK 8	162	24	1,630	,,	830

Making Methods.—The electrical porcelain section of the industry is called upon to supply a wider variety of shapes and sizes than any other section, while it also has to conform to more rigid specifications as regards size tolerances and performance characteristics. It accordingly makes use of the greatest variety of forming methods. Wherever possible, size tolerances are met by appropriate design of the article in the green state, due regard being had to different drying and firing shrinkages in different directions. When this is insufficient to achieve the desired object, forming of the article in the partly or completely fired state is the only solution. Most fired ceramic materials are so hard that grinding is the only feasible method. In the unfired or partially fired condition, cutting operations with steel or hard metal tools—the latter for long life—may be readily performed. Usually the equipment can be so designed that only one dimension of the ceramic needs to be accurate within fine limits.

DENTAL PORCELAIN

LITERATURE

W. Drum.—"Lehrbuch der Dental-Keramik." 1939.
H. J. Orlowski.—"Dental Porcelain." Ohio State Univ. Exp. Stn., 1944.
M. Maurice Picard.—"La fabrication des Dento Artificielles Minérales." *Bull. Soc. d'Encouragement pour L'industrie Nationale*, **119**, 523 (1913).
E. W. Skinner.—"The Science of Dental Materials." Saunders, Phil. and London, 1946.
P. Weikart.—"Leitfaden der Zahnarztlichen Werkstoffkunde." Hauser, Munich, 1950.
V. K. Ilg.—"Zahnärztliche Keramik." Munich and Berlin, 1949.

History.—**Pierre Fauchard** (1728) suggested the use of enamel. **Duchateau** (1774) used porcelain instead of ivory. Later **de Chaumant** suggested the addition of pipeclay to the porcelain, brought the industry to England, and in 1791 patented his process. In 1808 **Fouzi** of Paris used platinum pins for fixing teeth to the artificial plates. **M. Planton** in 1817 manufactured artificial teeth in America. England and the United States of America at present predominate in this manufacture. In the latter some 35,000,000 sets are made annually.

Manufacture.—Felspar and silica are ground to an impalpable powder, together with a certain amount of kaolin. The mixture is made into a thick paste, and is tinted a variety of colours by means of titanium oxide or by the use of salts of cobalt, uranium, manganese, etc. The paste is next pressed into moulds in which are inserted platinum pins. The teeth are then burned in saggers until well vitrified, a temperature of about 1,400° C. being required. They are then covered with an enamel made of the same materials as the body of the tooth, but mixed in slightly different proportions.

The composition of artificial teeth is that of a hard paste porcelain and they are manufactured in the same manner as the hard paste porcelains described on p. 186.

American dental porcelain is made from felspar 81 parts, aluminium silicate 4 parts, quartz 15 parts; German from felspar 73 parts, quartz 24.6 parts, marble 2.4 parts. In both cases a small amount of kaolin is added to opacify the mass. Orlowski gives results for teeth made with nepheline syenite instead of felspar as flux. They may be rendered fluorescent by small additions of uranium and thorium in suitable form.

In order to secure a satisfactory match with a patient's natural teeth, the dentist sometimes applies a small additional quantity of glaze of a suitable tint to the front of the teeth and refires them in a special muffle.

Owing to their greater lightness artificial teeth made from plastics are now proving a serious competitor for teeth of porcelain.

SECTION LXVIII

STONEWARE AND SANITARY WARE

By Alfred B. Searle
Consulting Technologist

LITERATURE

H. Ansell and A. B. Searle.—"Manufacture of Glazed Bricks and Sanitary Ware." London, 1929.
E. Bourry (translated by A. B. Searle).—"Treatise on Ceramic Industries." London, 1911.
W. Burton.—"English Earthenware and Stoneware." London, 1906.
A. Granger.—"Cèramique Industrielle." Paris, 1905.
M. Heim.—"Steingutfabrikation." Berlin, 1910.
B. Kerl.—"Gesammten Tonindustrie." Berlin, 1907.
H. Seger.—"Gesammelte Schriften." Berlin, 1908.
A. B. Searle.—"The Glazers' Book." (2nd edition.) London, 1948.
R. Newcomb.—"Ceramic Whitewares." New York, 1947.

A lengthy list of books and technical journals dealing with the manufacture of stoneware and sanitary ware is published in the following works:—

A. B. Searle.—"The Clayworker's Handbook." London, 1949.
M. Solon.—"Ceramic Literature." London, 1910.

The Transactions of the British Ceramic Society, *The Transactions and Abstracts of the American Ceramic Society*, *The Pottery Gazette*, *Claycraft*, and *Ceramics* frequently publish technical articles on Stoneware and Sanitary Ware.

The British Ceramic Research Association publishes papers and abstracts dealing with Stoneware and Sanitary Ware (for use of its members only).

Patents.—There are numerous patents connected with the manufacture of Stoneware and Sanitary Ware.

The term **stoneware** should strictly be confined to pottery whose chief characteristic is an opaque vitrified and an almost impervious body, but many articles described as stoneware have a porous body, and to some impermeable ware (such as porcelain) the term stoneware is never applied. Stoneware is, however, distinguished from porcelain by its opacity, *i.e.*, its lack of translucency, and from terra-cotta, earthenware, and faience by its almost impermeable body. Good stoneware should "ring" when struck; it should be too hard to be scratched by steel and should be highly resistant to acids.

The term **vitrified** refers to a material which has been heated sufficiently to become partially melted, the glass so formed then filling the pores. It does not mean that the whole has been converted into glass.

The finer varieties of stoneware have long been extensively used as pottery—as in the ware made by the Brothers Elers, John Dwight, Josiah Wedgwood, and Doulton & Co. For sanitary appliances, including drain-pipes, and for vessels resistant to acid used in various trades and chemical manufactures, a somewhat coarser stoneware is employed. The roughest kind of stoneware made is that used for paving stables and other areas where impervious blocks or tiles are required. Some years ago, when the demand for sanitary articles made of stoneware was much greater than the supply, a large number of firms used fire-clay for the manufacture of these goods, and placed articles with a porous body covered with a resistant glaze on the market as "stoneware." Hence the dual meaning of the term and a certain amount of confusion as to its true nature.

In recent years, stoneware has been increasingly used for plant employed in the manufacture of chemicals, for electrical and other insulators, and for other electrical equipment (switches, radiators and other heaters, etc.).

The chief object in making **sanitary ware** is to produce an article which will afford no resting place for germs, or from which germs can be readily removed.

So long as a glazed surface remains whole and the article is completely covered thereby, the texture of the body is of minor importance. Unfortunately, however, sanitary appliances are often used rather roughly, and are particularly liable to accidental blows which are strong enough to remove part of the glaze and to expose the body beneath; it is then impossible to keep such exposed portions hygienically clean unless the body is impervious to water and other fluids with which it is likely to come into contact. A porous body will absorb undesirable fluids and may become a serious menace to health, and for these reasons the demand for impervious stoneware for sanitary appliances tends to become stricter than it was some years ago. The present tendency is to specify ware with an impervious body for all better class work, leaving the ware with a porous body for instances in which cheapness is considered to be of great importance. In examining samples of stoneware as to its suitability for a given purpose it is, therefore, essential to consider the effect if a piece of the glazed surface were to be accidentally removed. It is, in fact, the slight damage to ware which must necessarily occur in its use which determines the necessity or otherwise of an impervious body.

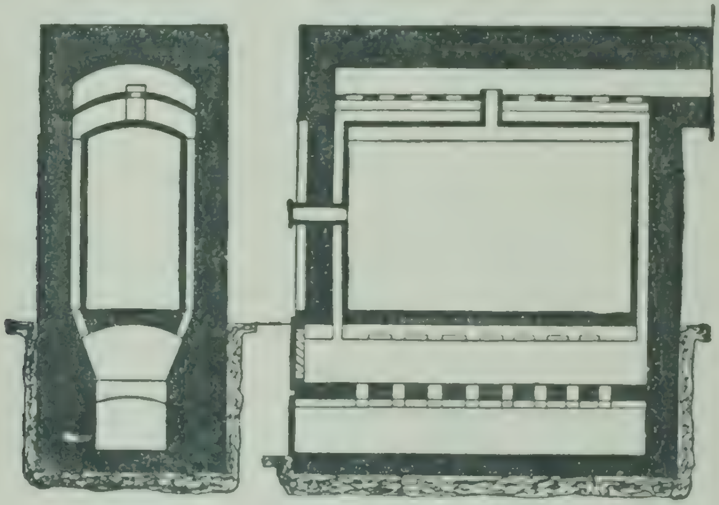


FIG. 1.—Sections of Muffle Kiln.

Fine stoneware, used for domestic pottery, vases, etc., is really a variety of porcelain which is more fusible and less translucent than what is commonly understood by porcelain. This finer stoneware is made by mixing ball clay, china clay, and flint with about an equal weight of Cornish stone, the ball clay being used to produce a highly plastic mass.

If the colour of the body is unimportant the whole of the china clay may be replaced by ball clay. In Wedgwood's Jasper stoneware a large proportion of barium carbonate was used in place of most of the Cornish stone just mentioned. The colour of stoneware may be due to impurities in the clay, or to cobalt or other oxides added to the body.

The great plasticity of stoneware paste enables it to be used in making many designs for which porcelain is entirely unsuitable; and the fine texture and close compact body possessed by fine stoneware has rendered it invaluable in the manufacture of pottery in which a sharply defined and complex shape is required. The texture and appearance of stoneware is such as to make this material more suitable for relief designs and decorative shaping, but some very beautiful colour effects can also be obtained. The size of the articles is usually limited by the tendency of the vitrifiable body to twist in the kiln, yet notwithstanding this limitation some very large articles have been successfully made in stoneware.

Fine stoneware is prepared, shaped, glazed, and burned in a manner so similar to that of earthenware (p. 179) that no further description is needed here. Where the ware will stand the high temperatures necessary, the use of a leadless glaze (including salt glaze, p. 211) is advantageous. Much fine stoneware is, however, unglazed, as the slight glaze formed on the surface by the vitrification of the body is sufficient for most purposes.

The greatest difficulty in manufacture is in the firing; if under-heated, the ware will have a porous body, but if over-heated it will twist or otherwise lose its shape.

Sanitary Ware.—As already explained, much of the sanitary ware now on the market, and in use in Great Britain, consists of a fire-clay or similar porous body covered with a leadless glaze. On the Continent, and to an increasing extent in this country, the use of a true stoneware is preferred.

The clay and other materials are crushed, mixed with water to form a soft paste, and then moulded in plaster moulds, chiefly by hand. After moulding, the surface is smoothed with wooden and steel tools, any supplementary parts are fastened on by means of clay paste, and the goods are set aside to dry.

Much attention has been paid to the production of sanitary ware by machinery, but with only a very limited amount of success. The articles made are so large that it is difficult to deal with them mechanically, and the variations in design, coupled with the enormous cost of such powerful presses, is against their extensive use.

A method of **casting** large pieces of sanitary and other ware which has rapidly sprung into favour (Weber's German Patent, 158,496) consists in the addition of a suitable alkali to the clay, agitating it mechanically with sufficient water to form a fluid slip, and then allowing this mixture to flow into a mould (see *Casting*, p. 182). By the use of a very small quantity—a fraction of 1 per cent.—of a suitable alkali (or baryta) a mixture of clay with a considerable quantity of grog[1] can be cast into vessels half-an-inch or more in thickness.

The use of alkali, including the use of baryta, for facilitating casting is very old, but its special adaptation to large vessels, and especially in connection with mixtures containing a large proportion of grog, is the subject of the patent by Weber mentioned above and of other patents.

Some makers burn them in this state and apply the glaze to the once-burned goods, but others apply the glaze to the unfired articles. There is much to be said for and against each of these methods; in some cases the first is preferable, and in others the second one is advisable.

The glaze is usually leadless, and may be (*a*) salt glaze, or (*b*) composite glaze. A **salt glaze** is not applied directly to the goods, but is formed by throwing salt into the kiln towards the end of the firing (see p. 211).

Salt glazing usually produces dark brown ware. It requires a temperature of at least 1,100° C.

A **composite glaze** is applied directly to the goods, either by dipping them into it, or by painting, pouring, or spraying it upon them.

There are many suitable glazes; one which is largely used consists of—

Cornish stone	3 parts.	Whiting	1 part.
Felspar	1 part.	Flint	1 "

When such a composite glaze is applied direct to stoneware the colour of the finished ware is commonly termed "cane," but in order to produce an agreeable tint it is usually necessary to add a little iron or manganese oxide to the glaze.

If **white ware** is required on a stoneware body, an intermediate slip or engobe is used between the stoneware and the glaze. This engobe is composed of white-burning clays, with sufficient Cornish stone or felspar to enable it to adhere properly. The white engobe effectually covers the coloured stoneware and makes the articles appear as if made of white clay.

---

[1] Grog is clay which has been calcined and then crushed to a coarse powder.

The use of engobes is accompanied by a number of difficulties, the chief of which are an irregular appearance of the surface and a tendency to peel or adhere badly. To avoid these, some firms of sanitary ware manufacturers add tin oxide to an otherwise transparent glaze, such as that mentioned above. By this means they produce a white opaque glaze, which serves the same purpose as an engobe and transparent glaze, with the advantage of better adhesion and appearance, and, in some cases, a lower cost of production.

Chemical and culinary stoneware is that used in the manufacture of acids and other chemicals, and for the preparation of food, etc. Its chief property is its ability to resist corrosion by chemicals, and to stand comparatively sudden changes in temperature. It is usually made of a natural clay without admixture, certain Dorset and Devonian ball clays being particularly suitable for the purpose. The clay must be carefully selected and prepared so that the ware may be uniformly vitrified. Where a suitable natural clay cannot be obtained, a more refractory clay is mixed with felspar, Cornish stone, or other suitable flux to make a stoneware.

The preparation of the clay is similar to that for bricks and tiles (p. 203), the material being crushed (if necessary) and mixed with water so as to form as uniform a paste as possible. It is pressed by hand into plaster moulds, or it may be worked on the potter's wheel if the shape of the ware permits. Great care is required to ensure the various joints being properly made, as some of the vessels made of this kind of stoneware are very complex in shape. Taps made of this material require special care in order that the parts may fit accurately.

Although properly made chemical stoneware is sufficiently impervious without any glaze, the cost of glazing is not great, and it gives a better appearance to the ware. It is effected by throwing salt into the kiln towards the conclusion of the heating. The salt is decomposed, and combines with the alumina and silica of the ware, forming a hard and impervious glaze.

Various kinds of kilns are used, but those of the rectangular or down-draught type (p. 229) are considered to be the best.

Remarkable improvements have been made in chemical stoneware in recent years.

Drain-pipes are used for the transmission of water and other fluids. In agricultural districts the ones used for land drainage are short pipes of porous clay placed several feet below the surface of the ground, but in towns the term "drain-pipe" usually refers to **glazed pipes.** The best glazed drain-pipes are made of vitrifiable clay or of a mixture of fire-clay and Cornish stone or other felspathic material, but a large number of such pipes are in use which have a porous body, and are made from a clay which has not been heated to vitrification.

If a true stoneware pipe (*i.e.*, one with an impermeable body) has the glaze removed from part of its surface, it is still as sound as before, but pipes with a permeable body readily "seep" or leak if damaged in this manner. Sanitary engineers are becoming increasingly stringent in their demands for pipes which will stand water under great pressure; it is not unusual to specify that each pipe must be tested by means of water at 100 lbs. per square inch pressure.

A vitrified body is invaluable when such tests are to be made, though many pipes with a porous body will, if properly glazed, stand this severe test very well. (For Tests, see ref. (2).)

Glazed pipes are usually made by crushing the clay or other materials to powder, mixing with water to form a stiff paste (see **Bricks,** p. 213), and then passing this paste into a pipe press, consisting of a vertical cylinder with an annular opening in its base, the size of the desired pipes. The clay entering the press is forced through this opening and the resulting pipe is cut by a wire to a suitable length and is removed. When socketted pipes are made a mould is fitted to the machine for that purpose.

The pipes are allowed to stiffen slightly and are then straightened and any inequalities in the surface are removed on a fettling machine which is a kind of lathe.

The **de-airing** of the clay before it enters the pipe press is very advantageous (see p. 237).

Various other types of pipe presses are in use, particularly for small pipes. The latter are frequently made in a brick machine of the "expression" type (p. 222), which has been fitted with a special mouthpiece. In this machine two or more pipes may be produced simultaneously.

Pipes of special shape, such as elbows, junctions, etc., are made by hand moulding or by cutting two or more pipes and fitting them together.

The pipes are dried carefully on floors heated by steam (p. 226), and are placed in round down-draught kilns (p. 229) to be burned. In these kilns, the pipes are stacked vertically one above the other, the smaller ones being placed inside the larger pipes so as to save space. Some skill is required in arranging the pipes so that the kiln gases can reach inside them, as otherwise they will not be properly glazed.

The earlier stages of the burning are similar to those in burning bricks (p. 228) or earthenware (p. 187), but the **Salt-glazing** is quite different. As soon as the pipes are sufficiently heated, the burner sees that his fires are burning brightly; he then lowers the damper, so as to reduce the draught in the kiln, and into the back of each fireplace he throws a shovelful of wet salt. The salt begins to decrepitate or jump about inside the kiln, and as soon as it comes into contact with silica or clay a combination of the sodium of the salt with the silica and alumina of the clay occurs, and a glaze is formed with evolution of hydrochloric acid fumes. The intense reaction which ensues causes a rapid drop in the temperature of the kiln, which must, therefore, be reheated in order that a uniform coating of glaze may be produced. It is usually necessary to treat the goods a second or even a third time with salt, the temperature of the kiln being raised between each salting.

If, during the salting, the kiln is heated under reducing conditions, the pipes will be darker in colour than if oxidising conditions prevailed throughout. The quantity of salt used varies with the arrangement of the goods, but averages about 1 oz. for each cubic foot of kiln space. It is important to observe that, for the production of a good salt glaze, the ware must be sufficiently siliceous and refractory; highly aluminous ware will not glaze well in this manner, and unless the ware is sufficiently refractory to stand prolonged heating at 1,100° C. or above, it is extremely difficult to obtain a good salt glaze. Sometimes a little borax is added to the salt to improve the glaze.

Glazed pipes are tested by plugging each end and pumping in water until the desired pressure is reached inside the pipe.

The pressure should be applied steadily, and should be maintained for at least an hour. Some engineers specify that the test must be made on several pipes joined together, and that the pressure must be maintained for twelve hours. Tests in which the pressure is increased until the pipe bursts are of little value; what is needed is a test which will show that the pipes are strong enough to resist any pressure to which they are likely to be subjected.

Paving blocks and tiles are used far less extensively in Great Britain than in America. This is partly due to the accessibility of suitable stone which can be crushed, made into concrete, and covered with a resilient mixture of tar, or bitumen and small stone, at prices sufficiently low to be attractive.

It has been proved by numerous "test roads" that properly made paving bricks are the most durable of any material except Aberdeen granite, and that they are far superior in this respect to macadamised roads. The relatively small extent to which they are used is due more to lack of initiative than to any inherent disadvantages.

For stable yards and other floors which require frequent washing, paving bricks form a durable material which is easily kept clean, and they are largely used for this purpose.

Paving tiles and bricks must be sufficiently hard to resist the abrasive action of traffic passing over them. They should be made of clays which vitrify readily and uniformly, as well vitrified clays form the strongest of all artificial stones.

Suitable clays occur in various convenient parts of Great Britain—particularly in Staffordshire and South Yorkshire—so that the Continental practice of adding a flux to a refractory clay is seldom, if ever, used in this country.

As the chief flux in the best clays used for paving bricks is ferrous oxide, it is advisable to fire the kiln under reducing conditions. All vitrifiable clays rich in iron compounds become more fusible when the iron is reduced to the ferrous state than when it remains as ferric oxide.

In all stoneware, but particularly in paving bricks and tiles, it is essential that the material should have a long range of vitrification. In other words, a considerable time must elapse between the commencement of vitrification and the point at which the goods begin to lose their shape.

Potash, soda, and lime are unsuitable fluxes as they cause a collapse too soon after the commencement of vitrification, whereas with magnesia and iron oxides the interval is much longer, and the pores in the goods may be completely filled with molten material without serious loss of shape occurring, providing that the temperature does not rise too rapidly. It is impossible to state very definite limits for these constituents, but a maximum of 2 per cent. of alkalis will generally be found satisfactory. The iron present may amount to as much as 15 per cent., and should not be below 5 per cent., expressed as ferric oxide.

The quality of the goods will depend on the texture and composition of the clay used, and on the skill with which they have been burned. It is essential that a sufficient proportion of coarse, refractory material should be present in order to form a support of skeleton for the fused material. If this refractory constituent is absent, or if it is spoiled by being ground too fine, the range of vitrification will be shortened, and the goods will collapse and twist.

In the best vitrifiable clays this refractory portion is usually in the form of relatively coarse grains of silica; to others a suitable proportion of crushed fire bricks may be added. If the refractory particles are too large they will prevent the material being properly vitrified, and it is therefore necessary to test very carefully any fresh clays which it is proposed to use for the manufacture of vitrified bricks, blocks, or tiles.

The colour of paving bricks and tiles may be pale yellow, as some of the Bytham bricks, but more frequently they are a bluish grey. "Staffordshire blue bricks" are typical vitrified bricks, though they are not—unless specially prepared—particularly suitable for paving purposes; with a little modification, however, paving bricks and tiles of the best quality can be made from the same material.

The "blue" colour is due to the reduced iron compounds combining with the alumina and silica in the clay, but its intensity is sometimes increased by the simultaneous deposition of carbon in the pores of the material.

The deep red paving tiles made at Ruabon, Accrington, in Staffordshire, and elsewhere are burned under oxidising conditions. They usually contain sufficient fluxing material to render any additional one unnecessary.

With the greatly increased use of concrete and of linoleum the use of tiles for domestic dwellings is much less popular than formerly.

Testing.—Paving blocks and tiles may be tested for porosity by weighing them, immersing them in water for some hours, wiping the surplus water rapidly from the surface, and re-weighing. The increase in weight will be due to the water absorbed by the pores, and may be expressed as a percentage of the weight of the original article, or preferably in terms of a percentage by volume.

Well made goods for paving should not show a greater absorption than 1 per cent. of their weight, and, preferably, the amount of water absorbed should be less than this. This porosity test is only of direct value as serving to distinguish non-porous from porous articles.

For testing the durability of the brick paving tiles in use, various methods have been suggested, though none of them are completely satisfactory.

In the United States—where many miles of brick-paved roads are in existence—the standard test consists in weighing a number of bricks, placing them in a drum with a suitable weight of iron balls, and rotating the drum for several hours. The bricks are then removed, fragments of less than 2 in. diameter are rejected, and the remainder is weighed. The loss of weight is taken as an inverse measure of the value of the goods.

Another test, largely used in Germany, consists in fixing a sample brick or tile just above a rotating plate containing sand. The amount of material ground away in a prearranged time is considered to indicate the durability of the article tested.

Both these tests are quite empirical, and their results are of only limited value.

REFERENCES

(1) British Standard Specification No. 1,257 (1945). "Standard Methods for Testing Bricks."
(2) British Standard Specification Nos. 65, 539, 540, and 1,143. "Properties and Tests of Drain-pipes."

SECTION LXIX

BRICKS

By Alfred B. Searle
Consulting Technologist

LITERATURE

B. Butterworth.—"Bricks and Modern Research." Crosby Lockwood & Son, 1948.
E. Dobson and A. B. Searle.—"Bricks and Tiles." (14th edition.) London, 1936.
A. B. Searle.—"Modern Brickmaking." (4th edition.) London, 1953.
—— "Clayworker's Handbook." London, 1949.
—— "Kilns and Kiln Building." London, 1916.
—— "Refractory Materials: their Manufacture and Use." London, 1917.
—— Cantor Lectures on "Brickmaking." 1911.
B. Kerl.—"Gesammten Tonindustrie." Berlin, 1907.
K. Dümmler.—"Handbuch der Ziegelfabrikation." Berlin, 1900.
H. Ansell and A. B. Searle.—"Manufacture of Glazed Bricks." London, 1929.
E. Bourry (translated by A. B. Searle).—"Treatise on Ceramic Industries." London, 1911.
R. B. Morrison.—"The Brickmaker's Manual." Chicago.

A lengthy list of books and technical journals dealing with the manufacture of bricks is published in "The Clayworker's Handbook."

The British Ceramic Research Association (Penkhull, Stoke-on-Trent) publishes frequent Bulletins to its members containing the results of recent research on bricks.

Patents.—There are many patents connected with the manufacture of bricks and before using any newly invented process commercially a careful "patent search" should be made to ensure that it does not involve an infringement of an earlier patent.

The literature relating to the manufacture of bricks is very extensive; the various machines and processes employed are now so numerous that they cannot all be described within the space available in the present volume.

Briefly, there are six chief groups of bricks: (*a*) Building bricks, (*b*) engineering bricks, (*c*) refractory or fire-bricks, (*d*) paving bricks, (*e*) glazed bricks and (*f*) lime-sand bricks.

Building bricks are of various shapes and sizes, the most important being parallelopipedons or prisms measuring about 9 in. × $4\frac{1}{2}$ in. × $2\frac{1}{2}$ or 3 in.

Bricks used for exterior work are known as **facing bricks**, and must be of pleasing colour and accurate in size and shape. For interior work, and where they are covered with plaster, stucco or rough-cast, less accuracy is needed, and colour is of little or no importance; such bricks are known as **common** or **stock** bricks,[1] and they constitute the greater part of the bricks manufactured at the present time.

For ornamental purposes, bricks of special shape are employed, for details of which the reader should consult works on building construction, or one of the treatises mentioned at the head of this section.

Building bricks are usually of a uniform red or buff colour, but some with irregular markings in blue and brown are much prized for special work. Stock or common bricks are usually very irregular in colour, no pains being taken to secure uniformity. Some of the Suffolk bricks are quite white.

---

[1] In some localities, stock bricks are considered as equivalent to facing bricks, and superior to common ones; in such localities they are the "selected" bricks—chosen on account of their superior appearance.

Most building bricks are very porous, and will absorb one-tenth to one-eighth of their weight of water on simple immersion, but bricks made in certain localities and by exceptionally powerful presses (as the Fletton bricks made by the "semi-dry" process) are much less absorbent on account of their dense surface. When specially light bricks are required they are usually made by mixing Kieselguhr or sawdust with clay; the sawdust burns out and leaves a very porous mass.

The chief characteristics of building bricks are strength, colour, and accuracy of shape.

The British Standard Specification No. 657 (1941) standardises the dimensions of building bricks made of clay, sand-lime, concrete, and composition. Three types of brick are specified; all are $8\frac{3}{4} \pm \frac{1}{8}$ in. in length and $4\frac{3}{16} \pm \frac{1}{16}$ in. in width: Type I is $2 \pm \frac{1}{16}$ in. thick, Type II is $2\frac{3}{8} \pm \frac{1}{16}$ in. thick, and Type III is $2\frac{7}{8} \pm \frac{1}{16}$ in. thick. These dimensions are chosen so as to allow mortar joints of suitable thickness with a standard distance of $9\frac{1}{4}$ in. centre to centre of joints.

Great variations in crushing strength are observable in bricks made in different parts of the country. These are partly due to differences in the clays, partly to the method of manufacture, and partly to the variation of opinion as to what constitutes "best quality" bricks.

The following table gives somes idea of the strength of some well-known bricks:—

Crushing Strength.	Tons per square foot.
London grey stock bricks	89
Suffolk white bricks (Gault)	135
Essex red sand stocks	96
Leicestershire red bricks (wire cut)	269
Fletton bricks (semi-dry process)	250
Staffordshire blue bricks	785
South Yorkshire bricks (stiff-plastic process)	540
Dutch clinkers (blue bricks)	587
Rubber bricks and cutters (very variable)	70

Some Local Authority By-laws stipulate that no bricks shall be used unless they have a crushing strength exceeding a specified minimum, which often varies with the locality.

Sound bricks can usually be distinguished by the clear, ringing sound they emit when two are struck together.

Engineering bricks are made of clays which become more vitrified when burned than do building bricks, and are consequently stronger than more porous bricks. Engineering bricks are used for bridges, reservoirs, and other important engineering structures where great strength is required.

They are usually blue or grey in colour, but some vitrified bricks manufactured in the Midlands, which are excellent for engineering purposes, are primrose tint. Staffordshire, Wales, and Accrington have long enjoyed the reputation of making the best engineering bricks in the United Kingdom, but smaller quantities of equally good quality are manufactured elsewhere. They closely resemble paving bricks (p. 211).

Refractory or furnace bricks are used when great resistance to heat is required. Their nature and manufacture are described on p. 245.

Paving bricks are described on p. 211.

Glazed bricks are usually made of a buff- or cream-burning refractory clay (fire-clay) as the application of glazes containing lead compounds to bricks is not wholly satisfactory, and the use of a porcelainous or felspathic glaze (p. 209) is scarcely possible on red bricks on account of their fusibility. The method generally adopted is precisely the same as for glazing sanitary ware (p. 200), the bricks—either in a raw or biscuit state—being dipped in a felspathic glaze, dried, and burned in a kiln at a temperature between 1,200° and 1,300° C.

There are ever-recurring attempts to purchase bricks ready-made and to glaze them, but such attempts must usually fail for one simple reason: in all glazed brickwork sharp edges are essential, and the greatest pains must be taken not to have the bricks chipped or damaged previous to the application of the glaze. It is, therefore, imperative that they should be made and glazed on the same works, as to cart them indiscriminately from one place to another would damage them irretrievably.

Attempts to glaze red bricks are almost equally unsatisfactory for another reason: it is exceedingly difficult to heat the whole of the bricks in a kiln uniformly, yet the limit of variation permitted by the glaze is such that it is almost impossible to obtain a sufficiently large proportion of well-glazed red bricks to make the process remunerative. With the harder glazes used on bricks made of fire-clay this difficulty is far less serious, as the variation in temperature permitted by the glaze is much greater than is the case with plumbiferous glazes. The argument that the temperature in potters' ovens varies as greatly as in a brick kiln is inapplicable, as the potter is able to arrange for a much greater variety of colours than can be applied to bricks, and the necessity for uniformity of tint and tone is not so great as in the case of bricks.

Sand-lime bricks are made by heating sand mixed with a small quantity of freshly slaked lime in an autoclave with steam under pressure. At the temperature reached in the autoclave, the lime combines with a portion of the sand and forms a cementitious silicate which binds the particles of sand together.

Sand-lime bricks are really a form of artificial sandstones and are referred to in the section on **Artificial Stones** (p. 139), being more fully described on p. 239.

The **raw materials** used for building bricks are the various clays, marls, sands and shales which occur in almost every part of England and Ireland. Stone occurs in such accessible forms in Scotland, that bricks are only used to a limited extent in that country.

Apart from the cost of preparation, almost any clay can be made into bricks, but this very facility constitutes a serious danger to the would-be manufacturer. Thousands of pounds have been lost through people with insufficient knowledge of the subject attempting to manufacture bricks from a material which is, in many respects, suitable, but for which the financial conditions are unfavourable. For this reason a consultation with a reliable and impartial expert—one who is entirely free from the obligations of selling plants or kilns of a particular design—is always advisable and usually saves much waste of money. Many instances of this might be given, but one must suffice: What is known as the "London clay" is largely an excellent material for the manufacture of bricks and tiles **provided that it is mixed with a suitable non-plastic substance**, such as sand. Alone, the London clay is extremely difficult to use, but in those parts of the country where it occurs in close proximity to a suitable sand it is a valuable material. Elsewhere it is of little or no value, as the cost of purchasing sand and carting it to the brickworks would be prohibitive. Failure to realise this has been the ruin of many brick manufacturers.

The characteristics of the various clays used in brick-making are very briefly outlined in the section on **Clays** (p. 149), but the reader who requires further details should consult the literature at the head of that section, and particularly the volume on "British Clays, Shales, and Sands" there mentioned.

Broadly speaking—though the special characteristics of certain earths make any general statement unsatisfactory—a material to be made into "clay" bricks should contain at least half its weight of true clay, the remainder being chiefly siliceous matter, so that its ultimate analysis will not show much less than 20 per cent. of alumina, nor above 75 per cent. of silica. It is, however, possible by the use of special processes to produce excellent bricks from almost pure silica, so that too much reliance must not be placed upon the figures given. It is only fair to remark that silica bricks cannot be manufactured by the same methods as those used for ordinary "clay" bricks, so that the figures mentioned are sufficiently accurate for most purposes, special cases being decided after a separate consideration of their individual merits.

Some clays are too rich in clay minerals to be satisfactory for brick making; these must be mixed with sand or some other suitable non-plastic material.

Very rich or "fat" clays shrink so much when made into bricks and dried that they crack and twist to an extent which makes their use without admixture almost impossible.

Of the various **impurities** in clays, the one most dreaded by the brick-maker is granular particles of **limestone**. These are distributed irregularly in some clays, and when bricks are made, burned and ready for use, the lime in them absorbs moisture from the air and, in many instances, will break the bricks to pieces. Bricks of this character may usually be recognised by the white spots distributed through them.

In order to remove the particles of limestone, various clay-cleaners have been devised, but they only take out particles of $\frac{1}{10}$ in. or more diameter, whereas particles as small as $\frac{1}{20}$ in. can do a large amount of damage to bricks containing them. The chief use of such clay cleaners is, therefore, to remove so large a portion of the limestone that the remainder will do but little harm. Three other remedies for this troublesome difficulty are in use: (i) heating the bricks in the kiln to such a temperature that the lime combines with the clay and forms an insoluble alumino-silicate, which is harmless; (ii) grinding the clay so that all the particles of stone will be so small that they can do no harm and (iii) dipping the bricks, as they come from the kiln, into water so as to quench the lime quickly before it has time to swell and break the bricks. There are obvious objections to these methods, and, wherever possible, clays containing granular particles of limestone should be avoided.

FIG. 1 (*a*).—Diesel-driven Excavator with Boom.

FIG. 1 (*b*).—Dragline Excavator.

(*By courtesy of Messrs Ruston, Bucyrus Ltd.*)

Chalk, on the contrary, is a useful constituent of some clays, and is largely used in the South of England in place of sand as a non-plastic diluent for the clay.

Red bricks owe their colour to iron compounds, the precise nature of which is not well understood. The red tint is commonly stated to be due to free ferric oxide in the clay, but this is improbable; if ferric oxide is the colouring agent, it must be produced as the result of some decomposition occurring in the kiln.

The addition of ferric oxide to clays to improve their colour has frequently been suggested, but the results obtained do not usually warrant the cost; moreover ferric oxide added in this way behaves in a very erratic and far from satisfactory manner.

Buff bricks are obtained by burning clays containing only a very small proportion of iron compounds, such as the fire-clays or the vitrifiable clays of Bytham.

White bricks are made of either natural or artificial mixtures of chalk and ferruginous clay; such mixtures are termed **malms** or **marls**, and the white colour is due to a reaction which takes place between the iron compounds and the chalk. The white bricks of Suffolk (made of gault clay) are particularly well known.

Preparation of Material.—Having obtained a suitable material, or one which is considered sufficiently suitable to warrant experiments on a large scale being carried out, the next question which arises is, "Which is the most suitable process for making this material into bricks?" A full answer to this question involves many considerations, the most important of which can only be judged by an expert. Hence, in the following pages no more than the barest outline is given of the various processes, and readers wishing for further information may consult the special books and treatises upon the subject, such as those mentioned on p. 213.

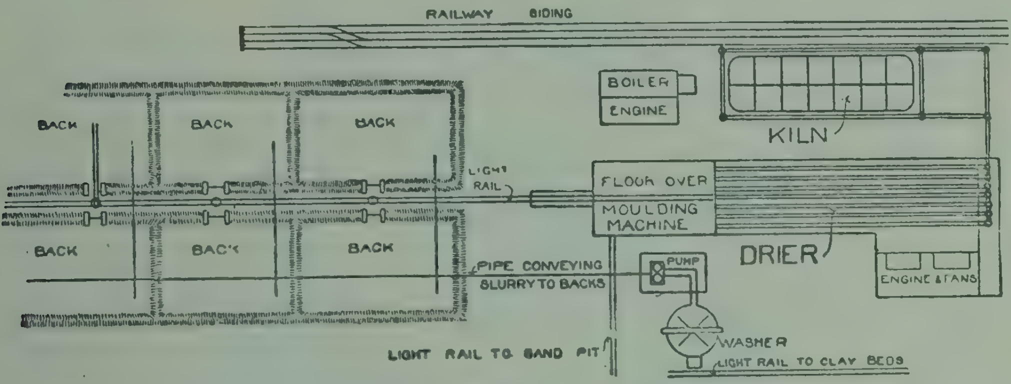


FIG. 2.—Arrangement of Washing Plant (after Middleton).

The clay for brick-making is usually quarried, but the "refuse" from coal mines is also used in some localities. It is seldom that clay for building bricks can be mined by underground methods at a remunerative rate. The clay is usually dug by hand labour (spade work) with the aid of blasting where the nature of the material permits. Where a sufficiently large quantity is needed, an excavator (Fig. 1) may be employed with advantage, as when worked at its normal capacity it will dig clay for about one-sixth of the cost of hand labour.

In many brickyards the clay is permeated by numerous seams or veins of unsuitable material, so that the digging requires skilled supervision and the use of an excavator may then be impossible.

As typical examples of the two extremes of clay-getting, mention may be made of the use of an excavator at the works of the London Brick Company at Peterborough, where a bed of Oxford clay, 20-60 ft. in depth, is dug and put into waggons at the rate of a ton a minute—and the ordinary small brickyard in the Isle of Wight, where the composition of the material completely changes every few feet, and, in some instances, layers of clay, sand, and other materials are found superimposed on each other (no single layer being more than a foot in thickness), thus necessitating the greatest care on the part of the men getting the clay, as some of the other materials would be very injurious were they allowed to enter into the composition of the bricks.

The uppermost layer or subsoil (frequently termed **callow** or **overburden**) must usually be rejected. As a whole treatise could be written on each of the chief methods of getting material for brick-making, whether by quarrying or by mining, and as a detailed description would take us too far from our main subject of the manufacture of bricks, we must assume that some sufficiently satisfactory method of obtaining a supply of material has been found, and now consider its treatment.

After the clay has been dug it may be sent direct to the plant or it may be set aside to enable the weather to act upon it. "Weathering" has a marked effect on many clays and shales, enabling them to be much more readily treated in the machines, and, in some cases, freeing them from undesirable impurities.

The demand for large numbers of bricks at economic prices has led to the discontinuance of weathering in many works; this is to be regretted, as in almost every case weathered clay makes better bricks than that which is used within a few minutes of its being dug.

The clay is next sent to the cleaning plant, if it is of such a nature as to require a rough purification. Two types of machinery are used for this purpose: the first consists essentially of a screen or riddle against which the pasty clay is forced; the clay passes through the perforations or slots in the screen, and the stones and gravel remain behind (p. 216).

Such an arrangement is obviously crude, and will not remove anything smaller than $\frac{1}{16}$ in. diameter, so that it is useless except for clays containing coarse impurities.

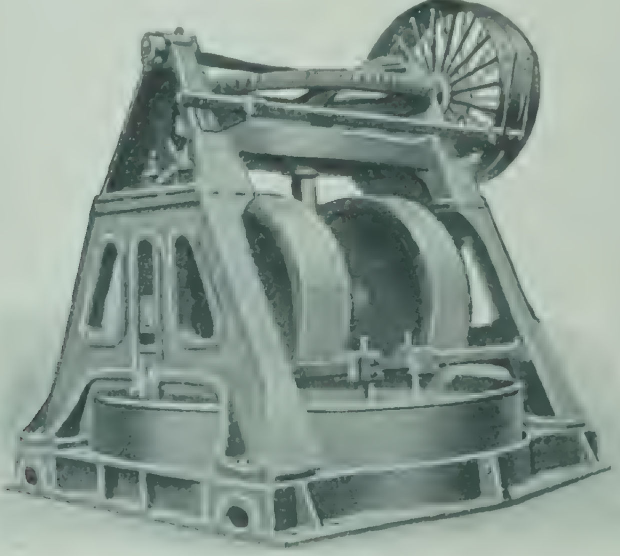


FIG. 3.—Edge-Runner Mill.
(*By courtesy of Messrs Sutcliffe, Speakman & Co. Ltd.*)

The second type of clay cleaning plant is known as a **wash mill**, and consists of a circular well in which a series of vertical harrows is rotated (see **Cement**, p. 87, Fig. 7). The clay is thrown into this well, a large quantity of water added, and the harrows set in motion so as to churn the clay and water together. After some minutes, the harrows are stopped, and the fluid portion is run off to large settling tanks.

The stones and gravel remain behind in the mill, and are removed when a sufficient quantity has accumulated. When a mixture of chalk and clay is used for brick-making, the mixing is usually effected in a wash mill.

The clay in the settling tanks gradually sinks to the bottom, and after a sufficient time has elapsed the clean supernatant water is run off, and the soft clay is cut into rough blocks and allowed to dry somewhat before being taken to the pug mill.

The cleaning or washing of clay is an expensive process, and is avoided wherever possible, but it is largely used in Kent and Essex (Fig. 2).

In some localities the clay is mixed with the siftings from domestic ashes partly to reduce the plasticity and shrinkage of the clay, and partly as a convenient means of introducing the fuel into the very centre of the bricks, and so secure as complete a burning as possible. This is the case with the clamp-burned stock bricks sold in London.

In most methods of brick manufacture, the raw material must be converted into a paste by mixing it with water. In the case of soft clays this is effected by means of a pug mill, but hard clays and shales must first be crushed or ground.

Clays may be crushed by (*a*) crushing rolls, or (*b*) edge-runners. **Crushing rolls** are usually mounted in pairs, and the clay or shale allowed to fall on top of them is passed between them and crushed in the process. If necessary, several pairs of rolls may be used, each pair being set rather closer together than the preceding ones, so as to effect a gradual reduction of the material.

Edge-runner mills resemble those used for mixing mortar, but are heavier and more powerful. They consist of two mill-stones which rotate on a horizontal shaft above either a fixed bed or a revolving pan. Perforations or slots in the bed or pan permit the crushed material to pass out of the mill into a receptacle beneath, from which it is raised by a bucket elevator to the screens. The coarse material is returned to the mill for further treatment, and the powder which has passed through the screen is taken to the pug mills or mixing machines.

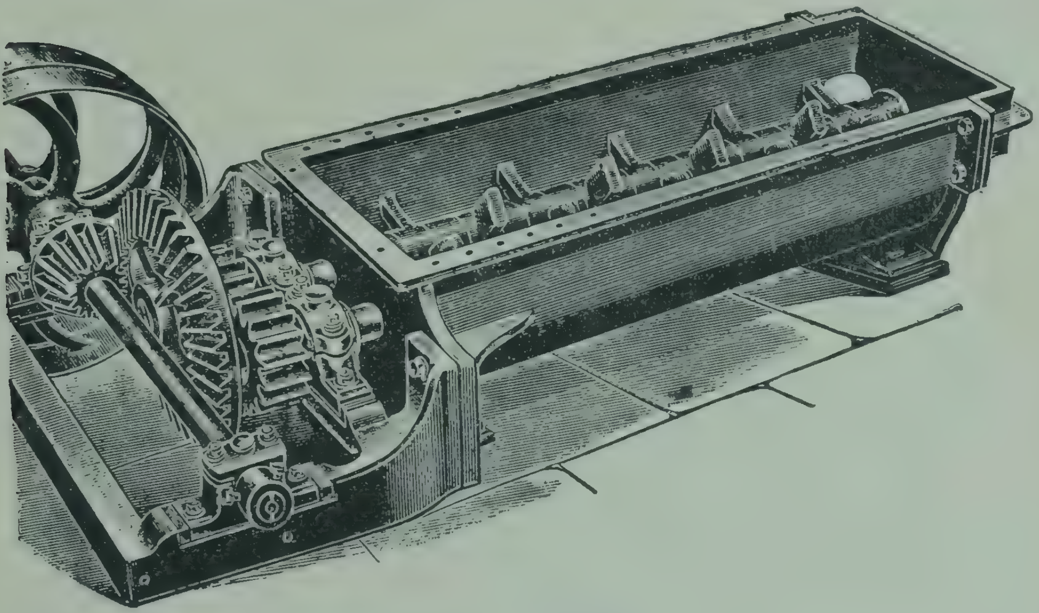


Fig. 4.—Open Mixer.
(*By courtesy of Messrs Whitehead & Co. Ltd.*)

If a clay is very tough it is sometimes necessary to pass it first through an edge-runner mill with large slots, and then through several pairs of rolls. Some shales and other rocks used for brick-making must be broken into small lumps in a stone-breaker before they are passed to the edge-runner mills.

Broadly speaking, tough, pasty clays are best reduced by crushing rolls, and shales or rocky clays are best treated in edge-runner mills, but each material requires separate study and must be dealt with accordingly.

Tempering is the term used to indicate the conversion of a clay or powdered shale into a homogeneous paste suitable for the manufacture of articles. It consists essentially in the addition of water and its thorough incorporation into the mass.

Tempering was, at one time, effected by men treading the material with naked feet, but the advent of mixing and pugging machinery has caused the abandonment of "treading," except in the case of crucibles for melting steel. Another method—still used in some out-of-the-way districts—consists in turning the clay over and over by means of wooden spades.

Two kinds of tempering machines are in use. The first is an open trough in which is one or more shafts carrying blades or knives set at an angle to it. Such a machine is known as an **open mixer**. A similar machine, but closed except for an opening at each end, is also used, and is known as a **pug mill**; in addition to mixing the clay and water it also compresses the material, and if the outlet end is made of a suitable shape—as when fitted with a **mouthpiece**—the clay paste issues from the machine in a compact column which can be cut into bricks.

In this way a pug mill serves not only as a mixer, but as a brick-making machine, and bricks so made are said to be produced by the "expression" or "wire-cut" process (p. 208). Where hand-moulded bricks are made the clay issues from the pug mill in so soft a state that no mouthpiece is needed.

Clays which are difficult to mix with water require the use of a long open mixer, followed by a pug mill of equal length and capacity, but for most of the south country clays used for hand-moulded bricks a single vertical pug mill is sufficient.

Pug mills may be of either the vertical or horizontal type, the former being generally used for mild clays and the latter—in conjunction with other machinery—for tough or hard clays.

Moulding bricks by hand is one of the earliest methods of manufacture, and it is still used very extensively in the South of England. In the Midlands and North, where the climatic conditions are less favourable, bricks are usually produced by mechanical means.

A brick mould consists of a wooden frame which is large enough to surround a freshly made brick. This mould has no top or bottom, and must, therefore, be laid on a table or bench when in use.

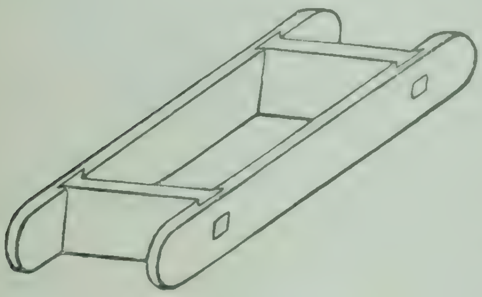


FIG. 5.—Brick Mould.

In **slop moulding**, the workman dips the mould in water so as to wet it thoroughly. He then places it on a prepared part of his working bench, and throws into it, with great force, a mass of clay paste rather more than sufficient to fill it. He next presses the clay well into the corners of the mould and removes any superfluous clay by drawing a straight piece of wood—termed a *strike*—across the top of the mould. He then, with a sudden turn of his wrists, lifts the mould with its contents and holds it sideways, and either hands it to a boy assistant or places it on a part of the bench ready for him. The boy carries the mould away to the drying floor or ground, and carefully placing it down, he empties out the soft brick without spoiling the shape.

In **sand moulding**, the interior of the mould is covered with sand instead of water previous to making each brick, and instead of a boy taking away the mould, the maker empties it on to a small board—termed a pallet—and a boy carries the brick away between two pallets to the drying floor. In addition to giving the bricks a pleasant appearance (sand face), the method of sand moulding is about four times as rapid as slop moulding, but cannot be used for all clays.

The bricks are carried on light spring barrows of special shape (Fig. 6).

One reason why brick-making machinery has made so little progress in some localities, is that a man and a boy can turn out 30,000 bricks a week by hand moulding, and this is sufficiently cheap for machinery to effect no appreciable saving where the clay is suitable for hand moulding.

If hand moulded bricks are required to be specially accurate in shape they are allowed to become partly dry, and may then be pressed in a portable press, operated by a strong youth.

The moulding of bricks by hand requires great skill, and as the work is also laborious, it is becoming increasingly difficult to obtain good moulders. This has led to the introduction of machinery to imitate the hand-made article, but such machines have never become really popular in this country. In the United States a large number of these "**soft mud**" machines are in use at the present time.

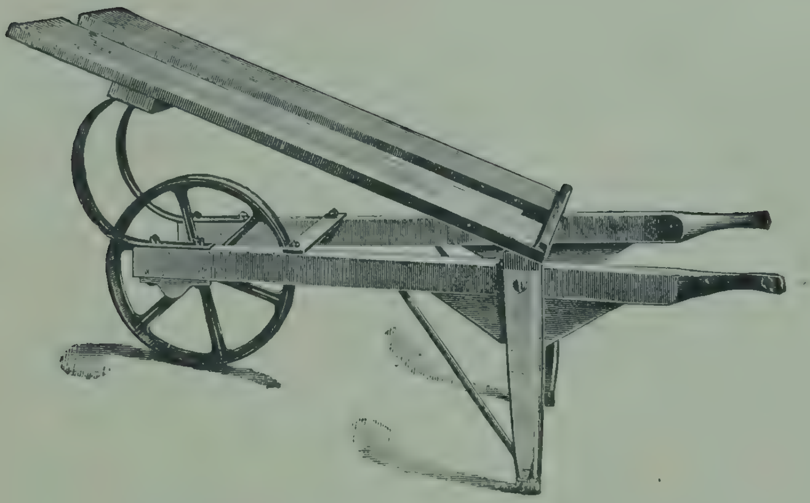


FIG. 6.—Barrow for Carrying Hand-Made Bricks.

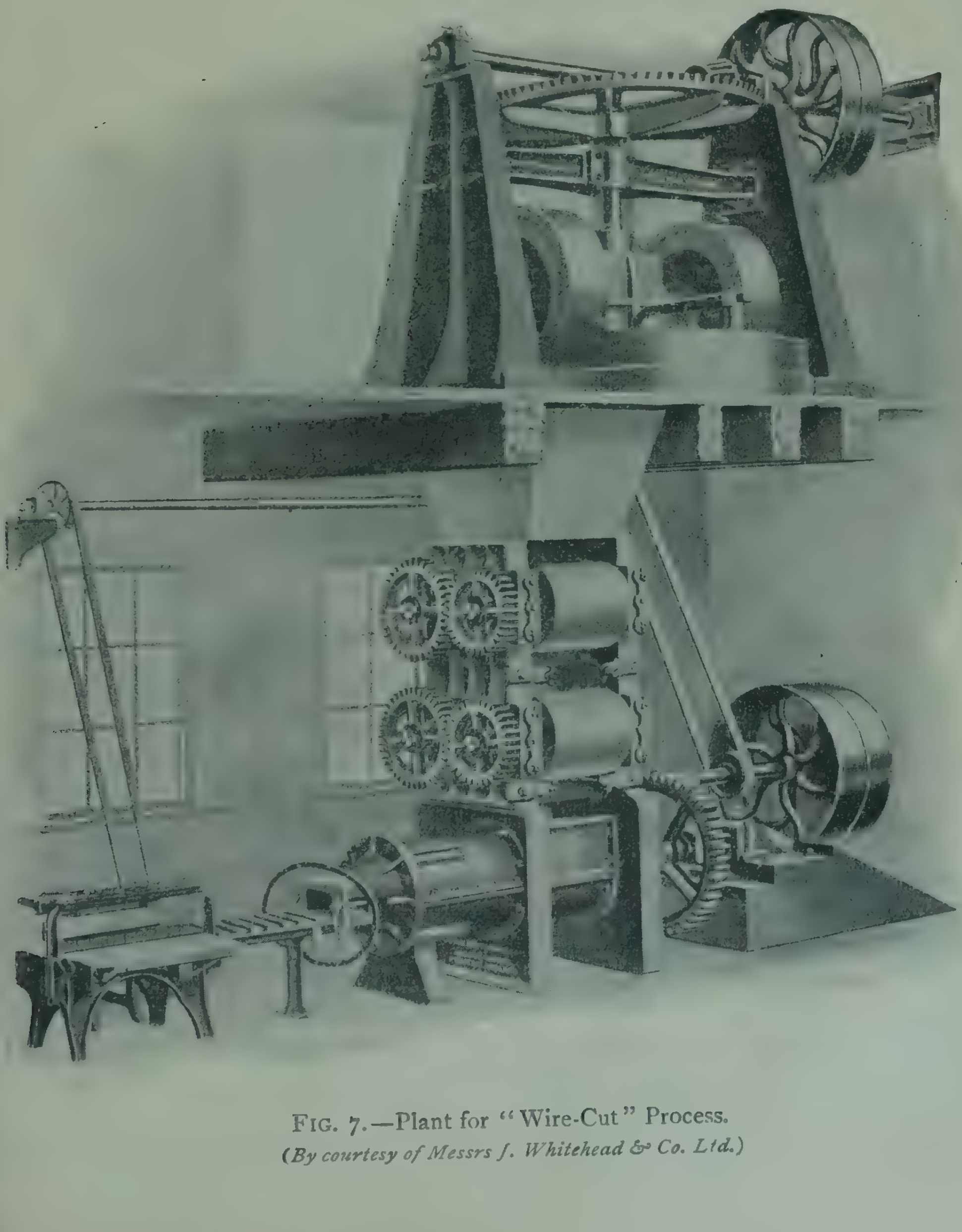


FIG. 7.—Plant for "Wire-Cut" Process.
(By courtesy of Messrs J. Whitehead & Co. Ltd.)

Most bricks made by machinery are produced by one of the following methods; (a) Expressing prepared clay through a die and then cutting it into bricks; (b) forming a preliminary clot or rough brick and repressing this to shape (stiff-plastic process); and (c) placing the moist powder or shale into a metallic mould and compressing it to shape in a powerful mechanical press (semi dry process).

The special advantages of processes b and c are to be found in the greater stiffness of the bricks produced by the machines. Owing to the water being present in only a small proportion, such bricks can be taken direct to the kilns without any previous drying. This materially reduces the cost of manufacture, but it must be observed that mechanically made bricks are very different in many respects from those moulded by hand.

Expressing clay through a mouthpiece attached to the end of a pug mill, and then cutting the extruding clay column cross wise into bricks, is a method of manufacture which can be applied to almost any clay capable of being made into bricks. As wires tightly stretched on a frame form the means whereby the clay column is cut, this method of manufacture is commonly known as the **wire cut process**. It is equally applicable to the production of pipes, hollow blocks, and a variety of other articles. As in the hand moulding method, the clay must be in the form of a soft paste, and as the column is usually cut into several bricks at a time, these are carried on a large board or pallet to the drying floor or on to the cars, which are then run into a drying tunnel. If desired, wire-cut bricks may be pressed after they have been partially dried.

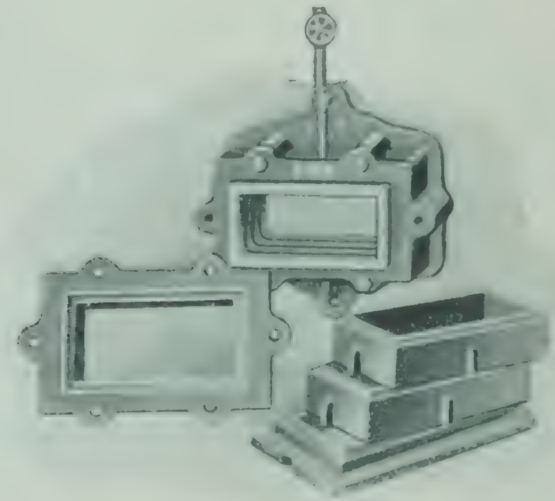


FIG. 8.—Mouthpiece—Assembled and in Pieces.

Where a clay is difficult to work by this process, the insertion of a pair of **expression rolls** between the pug mill and the mouthpiece will often facilitate the manufacture. These rolls also tend to reduce lamination and other troubles incidental to the wire-cut process when it is applied to some clays. De-airing the clay will also improve its workability (see p. 237).

In the **stiff-plastic process** of brick making, the clay paste must be very much stiffer than for hand moulding, and as such a paste is difficult to obtain with some clays, the stiff plastic-process has been most successful when applied to shales and other dry clays which are capable of being reduced to powder. This powder is then mixed with a very small proportion of water in a powerful pug mill, and the stiff paste is forced into a clot mould which makes it roughly of the desired shape.

Various ingenious devices have been patented for producing the clot or rough brick, but only two are now extensively used. The first of these consists of a horizontal steel disc or table fitted with moulds; the clay is forced into one of these moulds by means of a fixed vertical pug mill and the table then makes a partial rotation, placing an empty mould beneath the pug mill. After the table has rotated sufficiently, one of the moulds is emptied automatically by means of a rising plunger, and the clot is then ready for the repress. This arrangement is the basis of the Bradley & Craven brick machine (Fig. 10).

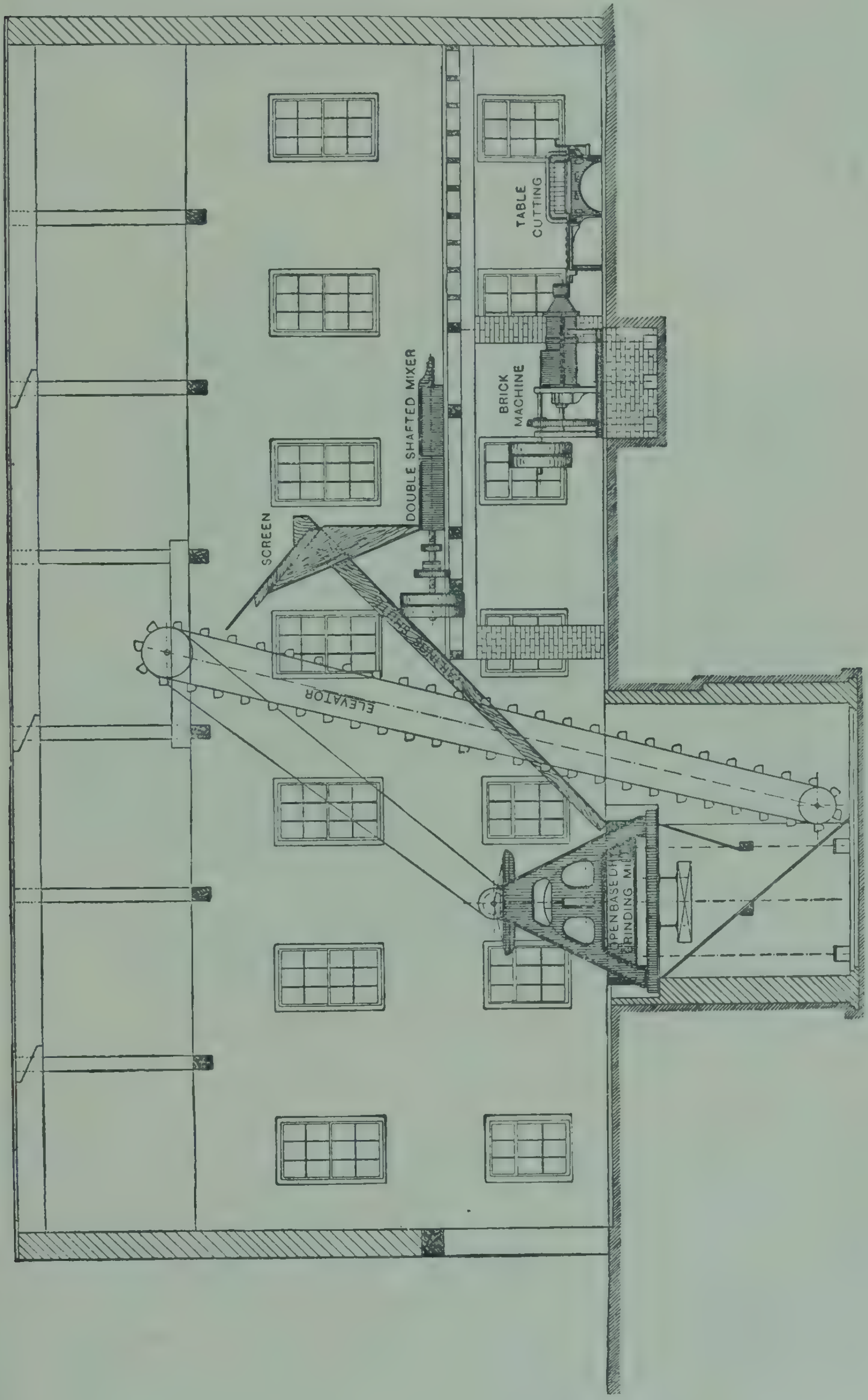


FIG. 9.—Plant for Making Plastic Bricks from Dry Clay or Shale.
(*By courtesy of Messrs J. Whitehead & Co. Ltd.*)

The second method of making a clot from stiff-plastic clay consists in forcing it with a ram or pug mill into the spaces between the cogs of a specially shaped wheel, these spaces forming the clot mould, and temporary ends being formed by the framework in which the wheel revolves. As the wheel revolves, the clay in the mould is eventually raised to the level of the repress, and the clot is pushed out sideways by means of a lever which takes it direct to the press. This arrangement is the essential feature of the machines made by T. C. Fawcett Ltd., and R. Scholefield respectively (Fig. 11).

As the clots are only roughly shaped, it is necessary in each case to employ a press in connection with the clot mould, and the machines mentioned are so arranged that powdered clay is delivered into one part of the machine and the properly pressed bricks are obtained from another. This is effected by combining a pug mill, clot mould, and press in one framework.

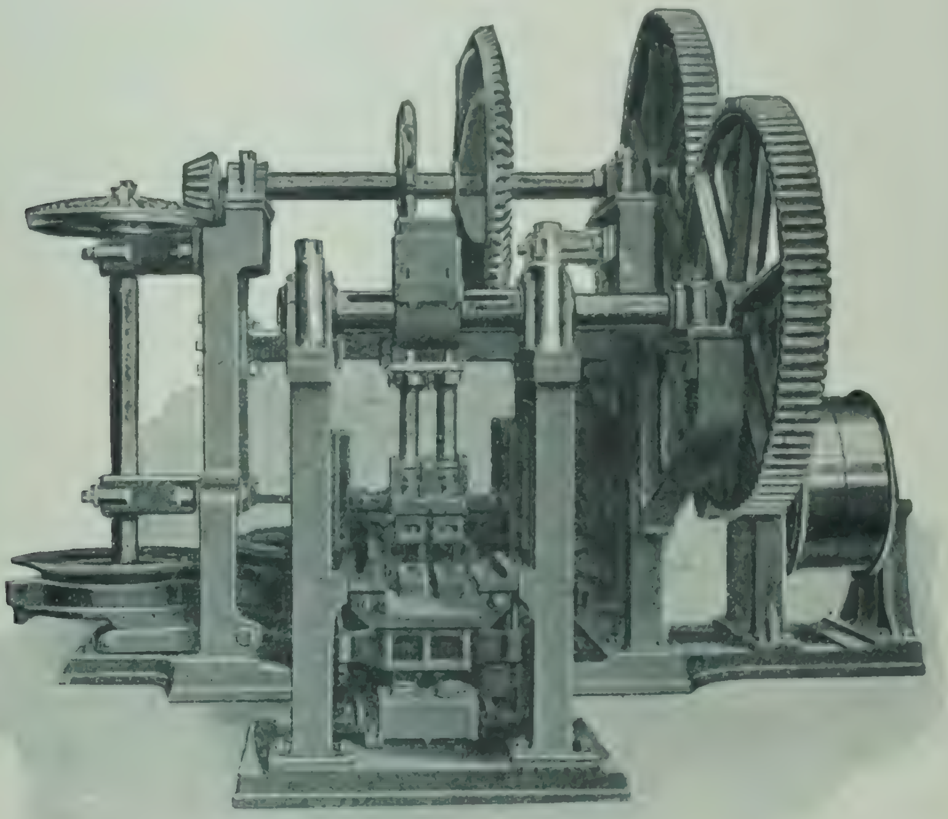


FIG. 10.—Machine for Making Bricks by the Stiff-Plastic Process.
(*By courtesy of Messrs Bradley & Craven Ltd.*)

Although the final pressing in a stiff-plastic machine really constitutes a repressing of the clot, some makers use an additional repress machine for the manufacture of facing bricks, the bricks being passed into this immediately after leaving the ordinary machine or after they have been partially dried. Unless, however, the material is peculiarly difficult, it is unnecessary to subject them to this treatment. If, through lack of adjustment, the machine produces unsatisfactory bricks, it is better to adjust the machine rather than to give the bricks additional pressings, though with some clays this cannot be avoided.

The average output of a stiff-plastic machine is 10,000 to 12,000 bricks per day of ten hours.

The stiff-plastic process, whenever it can be properly used, is the most satisfactory of all methods of brick-making, as it combines most of the advantages of the fully developed plastic clay, with a reduced cost in drying the bricks. Stiff-plastic bricks may go direct into continuous kilns, but it is usually better to dry them first in a tunnel drier, or on a steam heated floor, as the moisture is then more satisfactorily removed than in the kiln, and the loss by improperly dried bricks is much less.

The Semi-Dry Process.—Where the material is sufficiently dry to be in the form of a powder which readily "balls" on leaving the grinding pan, it is often economical to work it up without any addition of water at all. As the material is not completely dry, this process is known indifferently by the terms "semi-dry" and "semi-plastic," both being equally unsuitable, but used in the absence of more accurate terms.

Bricks made by this process are quite distinct in character from those in which the plasticity of the clay has been more fully developed, and though they were much used a few years ago, they are rapidly being displaced (except for common work near London) by stiff-plastic bricks.

Where the material is of a suitable nature, the semi-dry method of working effects marked economies in the cost of production, as it dispenses with the cost of pugging and drying, and the friction of the material in the plant is also materially reduced. Against this must, however, be set the added power required to compress the material into bricks; this, in some instances, being very great.

The semi-dry process is carried out in its most perfect form in the neighbourhoods of Accrington, Peterborough, and Bedford, where a suitable material extending to great depths is found in such large quantities as to facilitate the manufacture of bricks on a colossal scale.

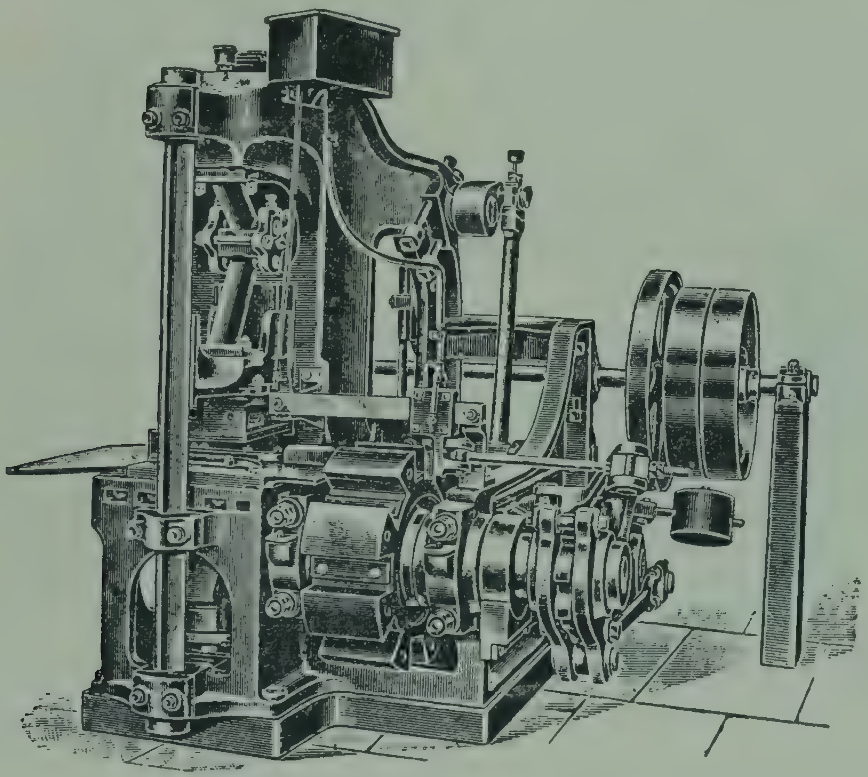


FIG. 11.—Machine for Making Bricks by the Stiff-Plastic Process.

(By courtesy of Messrs T. C. Fawcett Ltd.)

To be worked to advantage the material must be cleared of surface soil, or "callow," and must be then worked vertically, so that several strata may be mixed together in definite proportions. This is best effected by using powerful steam or electric navvies, which are capable of excavating a ton of material at a single stroke. The material is then taken in waggons to the grinding pans, and the fine product is separated by means of screens. It is then carried away by conveyers or belts, which mix it and convey it simultaneously, the coarse material being meanwhile returned to the mills to be reground. The powder falls down a small chute to a powerful press, which fills first a sliding feed-box, and thence the first mould. The amount of material received into the mould can be instantaneously adjusted to allow for variations in the moisture in the material. The pressure is applied through descending plungers, the driving mechanism being so arranged as to give two distinct nips or pressures on the bricks.

The object of this is to liberate as much air from among the particles as possible, so that when the final pressure of not less than 80 tons is exerted, there may not be any air imprisoned, as this would cause cracks in the bricks.

It is necessary in Peterborough to repress the bricks, so that four distinct pressures are applied, viz., two in the first mould and two in the second.

Bricks made in this way are so dry that they may safely be taken direct to the kilns and burned in the ordinary manner.

The chief advantages of this process, for shales and other hard material, are the great pressures which may be employed, whilst yet using less power than is needed in other processes, the absence of drying arrangements and consequent saving in fuel, and the accuracy in the shape of the bricks. As these are not plastic, they shrink so little in burning that there is but little liability of twisting or warping. The disadvantages of this class of brick are their surface density, which often makes them difficult to lay rapidly, as mortar does not readily adhere to them, the absence of a peculiar texture to which plastic-made bricks owe their durability, and the difficulty experienced in obtaining a perfectly sound brick which is of equal density and strength throughout.

This last-named defect is specially characteristic of semi-dry bricks, and though many attempts have been made to remove it, there is no machine at present in use which entirely overcomes it with certain clays, which otherwise appear to be quite suitable for manufacture by this process.

From the foregoing very brief descriptions it will be seen that the method to be employed in shaping the bricks must depend very largely on the nature of the clay, a plastic clay requiring a treatment quite different from that which is best suited to a shale or hard clay.

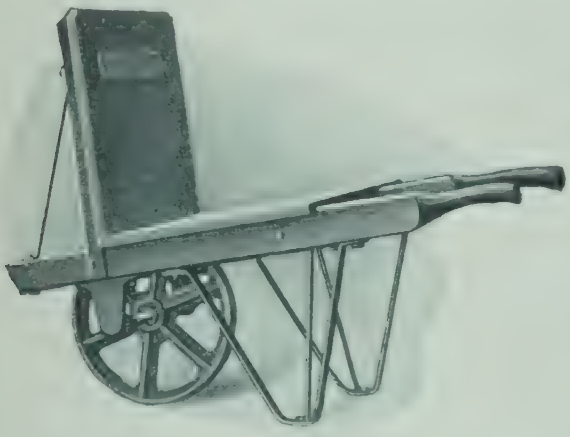


FIG. 12.—Barrow for Carrying Machine-Made Bricks.

In order to meet the requirements of clays in various localities numerous patterns of machines are in use, but for a fuller description of these the reader may refer to "Modern Brick-Making" (see Literature on p. 213).

Machine-made bricks are carried on stout barrows similar to that shown in Fig. 12 or on self-propelled trucks.

Drying.—As already explained it is usually necessary to dry the bricks before they can be placed in the kilns. The necessity of a careful and thorough drying becomes more apparent when it is realised that from plastic brick at least 1 lb. of water must be removed.

Articles made of clay are so delicate before they are burned, and are so sensitive to draughts and sudden changes in temperature, that they must be dried with exceptional care. In many parts of the country the bricks are stacked in long rows or hacks in the open air, and are protected from the direct rays of the sun and from the wind by covering boards, and by cloth, hurdles or loo boards placed along their sides. If carefully treated, many bricks may be dried satisfactorily at very little cost, but the process is very slow—requiring several weeks—and the uncertainty of the climate is also a serious disadvantage.

Where bricks are made by machinery, it is usual to dry them by artificial heat in a building constructed for the purpose, and termed a **drier**. Some driers consist merely of large sheds, beneath the floors of which are flues heated by coke or steam. The bricks are laid on the floor, and the latter is then heated gently at a rate suitable for the particular clay in use. This arrangement is quite satisfactory for most clays, but is slow, requires a large amount of space, and consumes a considerable amount of fuel. If, however, the floor is heated by exhaust steam, the last named consideration is of little importance.

Where the output is sufficiently large, bricks may be dried more expeditiously, with less loss and with less fuel, by passing them through a **tunnel drier**. This consists of a wooden or wood and brick structure of great length, which is just large enough to hold a series of cars loaded with the bricks to be dried. Warm air is drawn into this tunnel by means of either a chimney or fan, and is distributed in such a manner that the bricks are dried as rapidly as possible with the least risk of cracking.

In the best forms of tunnel drier, the bricks are dried (*a*) by contact with warm air circulating through the tunnel in a prearranged manner, and (*b*) by radiation from a false ceiling and from the heated walls and pipes in the tunnel.

The construction of tunnel driers is in itself simple, but with delicate clays so many matters have to be taken into consideration as to make the designing of a really satisfactory tunnel apparatus a matter of great difficulty. Consequently, there are many tunnel driers in use, but only a small number of them work with reasonable efficiency. This is largely due to the principles underlying the physics of drying bricks being very imperfectly understood by most brick manufacturers and builders of driers. The physical changes which occur in drying bricks are highly complex, and until they are better known than is at present the case, an "ideal" drier cannot be designed. Nevertheless there are at least two patterns of tunnel drier in use, which appear to meet all requirements except that they are costly to instal and troublesome—though not expensive—to maintain.

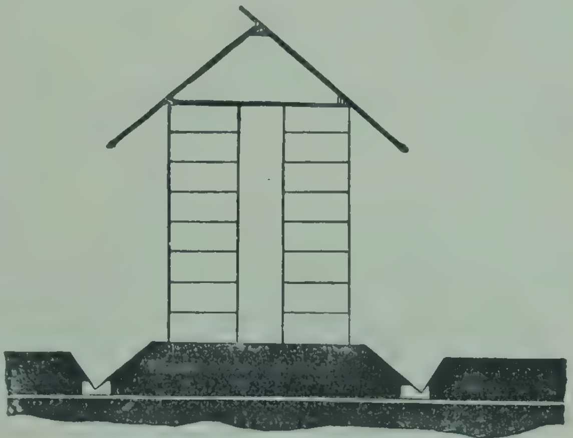
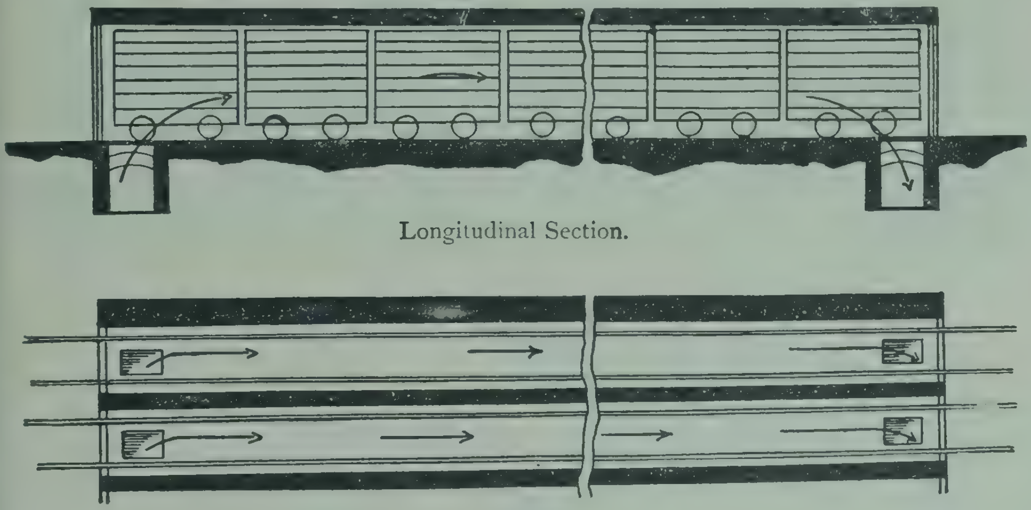


FIG. 13.—Hack or Open-Air Drier.

In drying bricks it is essential to bear in mind that the interior must dry at the same rate as the exterior ; any reversal of this will usually result in cracked bricks.

The difficulty is commonly found in heating the interior of the bricks sufficiently for the water in them to be vaporised without, at the same time, drying the exterior at such a rate as to cause cracking.

The use of warm air containing a definite and regulable proportion of water appears to be the best solution of the problem, and is an important feature of all the most successful forms of tunnel drier.



Longitudinal Section.

Plan.

FIG. 14.—Tunnel Drier.

All bricks have two critical periods during the drying : the first is during the removal of the first portion of the water—when the outer particles tend to shrink more rapidly than those in the interior and so cause surface cracks ; and the second is when the bricks have a hardness about equal to that of leather. In the latter stage, they are often exceptionally sensitive to sudden changes in temperature, and to draughts, and also to too rapid heating. Many existing tunnel driers cannot be worked at their full capacity with certain clays because of their inability to deal with this second stage in the drying, and it will usually be found that only those driers in which the current of air travels in the same direction as the bricks are satisfactory in this respect.

The great advantage of all tunnel driers is that the goods are taken from the brick machines and are placed on cars; these cars then travel slowly through the drier, and eventually reach the kiln, without any direct handling of the bricks being necessary.

In one modern form of drier the bricks are placed on loose shelves one above another and remain stationary in a current of warm air. The loading and unloading of the drier is effected by a special kind of truck which is loaded automatically.

Burning.—Bricks which have merely been dried are too friable and weak to be of value. The object of burning them is to convert this weak mass into a strong stony one, which is capable of resisting all kinds of weather.

It should be noted that when bricks "baked" or heated to a point where the plasticity is destroyed, but not sufficiently for many of the particles to fuse and, on cooling, makes a strong cementitious mass, the bricks are more durable and porous and are useful for certain purposes, but they will not last as long as those which have been properly burned, *i.e.*, in which the heating has been carried to such an extent that the finished bricks consist of certain rock-like particles firmly bound together by a species of slag or glass. Such vitrified bricks are much valued by engineers on account of their great strength and durability, but for ordinary buildings their lack of porosity makes them difficult to lay, and many bricklayers therefore object to use them.

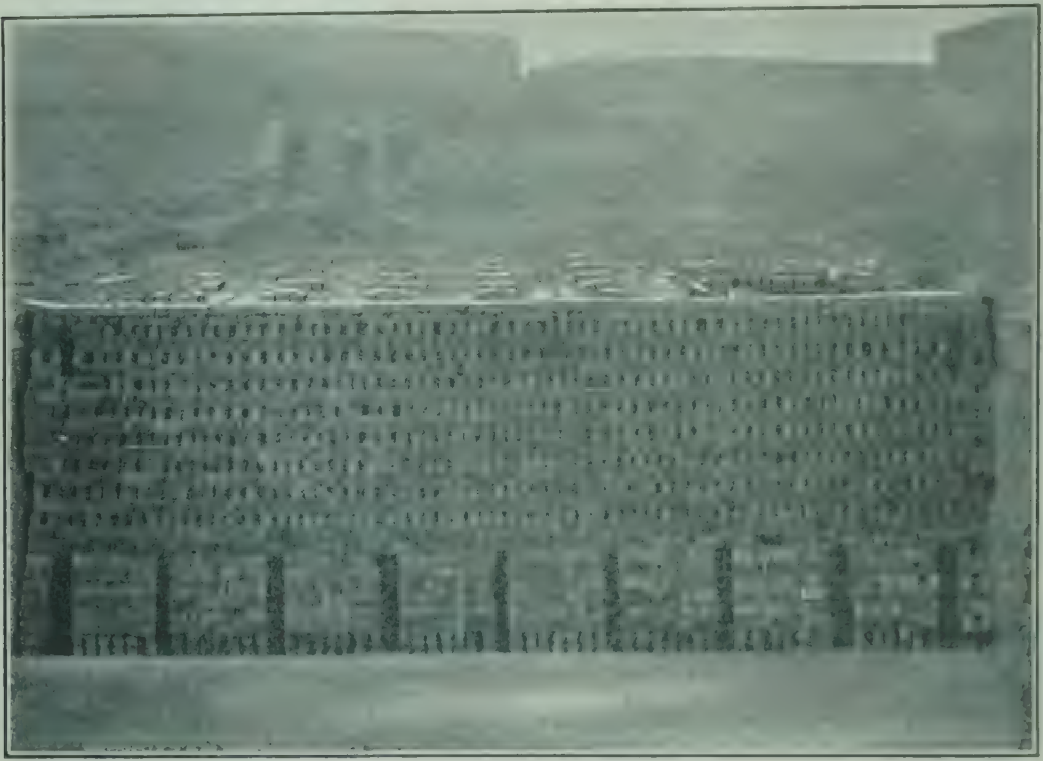


FIG. 15.—Archless Kiln.

(*By courtesy of Mr H. Harrison.*)

When a clay is worked up in a plastic condition, there is not the same necessity to burn it completely, as the bricks are usually strong and durable enough without this, the fineness of the particles and the felting nature of the clay being sufficient; but shales, rock-clays and other materials in which the plasticity has not been fully developed in the manufacture into bricks, require to be very fully burned in order that they may derive from the vitrified material the strength which they do not otherwise gain owing to their lack of plasticity.

The temperature to which a given brick must be heated in order that it may be satisfactory depends, therefore, on the nature of the material, the method of manufacture, and the purposes for which the brick is to be used. For example, a brick which is to be rubbed down to a particular shape, as in the construction of arches, etc., must be sufficiently soft for this treatment, and cannot be more than baked, whilst an engineering brick must be as hard and strong as possible. It is useless, therefore, to attempt to determine a standard temperature at which bricks shall be fired, and each brick manufacturer must decide for himself the one most suited for his customers' particular needs.

Kilns.—In consequence of the great variety of properties required in bricks, it is necessary to burn them in different ways, and, therefore, to use different types of kilns.

At the present time, there are so many patented kilns for brick-burning that even a list of them would be too lengthy to be given here, and many of these patents contain ideas and features of little or no commercial value. (Details are given in some of the volumes mentioned on p. 199.)

At the same time, there are certain kilns which are of the greatest importance, and the improvements in bricks during the last thirty years, and especially in the great reduction in cost of high quality bricks, is due in great measure to the modern types of kiln now in use.

At the present time, there are five distinct types of kiln in use for brick-burning, each with its special advantages, and the brick-maker must choose according to his technical requirements and to the capital at his disposal. If his works are small, with an output of less than a million bricks per annum, he may not have sufficient output to erect a fuel-saving kiln, and must be content to suffer the disadvantages of a high cost of manufacture and burn 10-18 cwt. of coal, where, with a better kiln, 3-5 cwt. would suffice. It is commonly argued by many brick manufacturers that only a certain type of kiln can be used for their bricks, but a large experience as a consultant in brick manufacture has convinced the author that this is incorrect in most cases, and that if the output is sufficiently large to justify its erection, one of the more recent continuous kilns, in which a minimum of fuel is employed, can be used for every kind of brick and architectural terra-cotta now on the market, with a saving of 30-70 per cent. of fuel as compared with single kilns.

Great care is, however, necessary in the selection of a modern fuel-saving kiln, as several are now in use which are comparatively worthless, because the money laid down, plus the cost of repairs, overbalances the saving effected in the fuel. This is particularly the case with kilns which are too short.

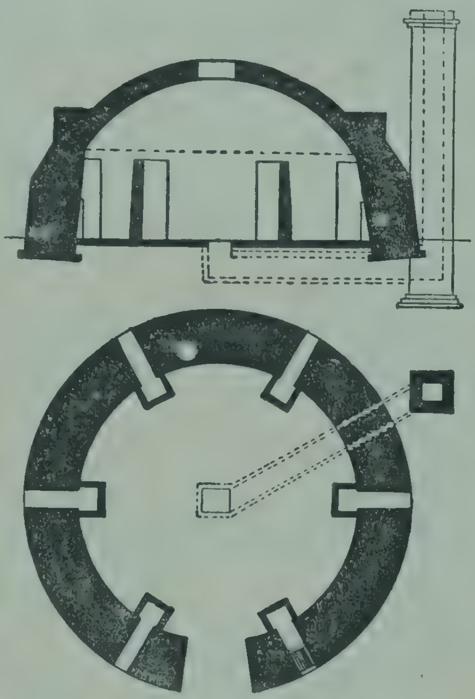


FIG. 16.—Cross Section of Round Down-Draught Kiln.

In out of-the-way districts, and for temporary purposes, the simplest form of kiln is that known as a "**Clamp**." This consists of a structure of unburned bricks and fuel, the latter being placed at the base, or, alternatively, between the courses of bricks. The bricks are so arranged that sufficient air can pass between them to burn the fuel and for the resulting hot gases to heat the bricks sufficiently.

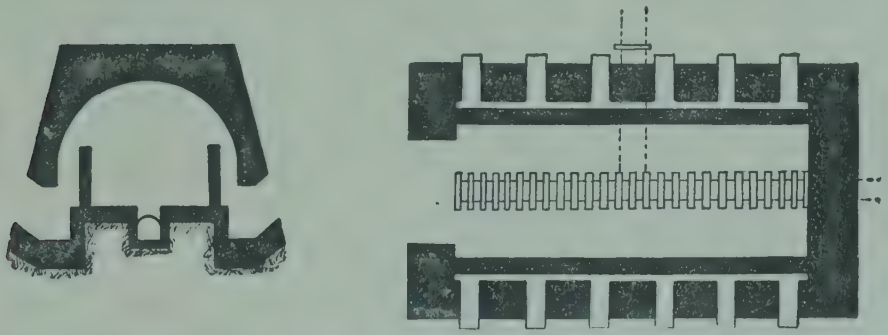


FIG. 17.—Cross Section and Plan of Down-Draught Kiln.

In such a kiln, the temperature is very irregular, but if the bricks are properly arranged it is not difficult to obtain a sufficiently large proportion of saleable bricks to meet local needs. Where a better brick is required, however, some form of kiln in which the bricks do not come in contact with the fuel, and in which the heat is under better control, must be used.

The construction of a clamp kiln requires so much skill that a detailed description of it is undesirable at this time, especially as this kind of kiln is chiefly used for temporary work, and equally good, and often better, results may be obtained by constructing an **archless kiln** (Fig. 15) and substituting a fan for the ordinary chimney.

Such a kiln can be erected at a very small cost, and whilst the product is not so good nor the kiln so durable as when properly covered in, the bricks are more evenly heated than in a clamp, and are as saleable as common bricks in almost any district.

Single kilns are much used for brick burning (Fig. 17). In these, the fuel is burned in special fire-boxes or furnaces, the hot gases passing through and around the bricks and heating them to the desired temperature.

Single kilns may be of three types, according as the general direction of the flames is upward, downward, or horizontal when in contact with the goods. **Up-draught kilns** usually have several fireplaces at each side or somewhat beneath the floor, whilst the chimney (if one is used) is at the top of the kiln. Up-draught kilns for bricks may be either circular or rectangular in shape, the latter being preferable, as they may be built of almost any capacity. In their simplest form, they consist of a space enclosed by one circular or four straight walls, the bricks to be burned being placed within the space in such a manner that the hot gases from the fires ascend through them and out at the top of the kiln.

Some up-draught kilns are covered with permanent brickwork on which a short chimney or series of chimneys is erected. As the heat enters the kiln through the fire-boxes, which are placed some distance apart, it rises irregularly in a series of different streams which do not completely mingle and consequently the goods are irregularly heated.

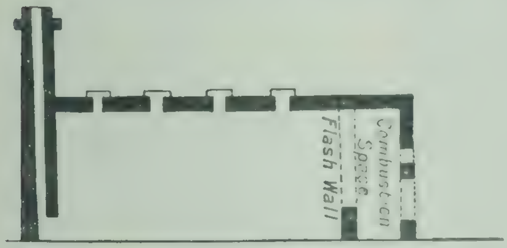


Fig. 18.—Newcastle or Horizontal Kiln.

In **down-draught kilns**, the general construction is similar, but the hot gases and flames first rise through an annular space to the top of the kiln, and are deflected downwards on to the bricks to be burned, spreading themselves fairly evenly throughout the mass, and passing through a central "well" or other openings in the floor to the main flue, and thence to an independent chimney (Figs. 16 and 17).

The heating of such a kiln is much more regular than that of an up-draught one, and some of the best bricks ever made have been produced in kilns of this type. Their chief disadvantage is the amount of fuel required per thousand bricks burned, which is seldom less than 8 cwt., and is often much higher than this. Consequently, they are being rapidly replaced by continuous kilns in which the gases, after heating one set, are used for heating a further set of bricks, more and more bricks being used until the temperature of the gases is reduced to a point below which it is useless to employ them. Even in such a kiln, the principles of the down-draught type may be utilised in almost their original form, and for the best facing bricks the most suitable kiln for large outputs is virtually a series of down-draught kilns connected together so as to make the fullest possible use of the heat in the fire-gases.

Horizontal kilns (Fig. 18), with the fires at one or both ends, the flue gases being taken away at the centre, or at the end opposite to the fires, are much used in the neighbourhood of Newcastle.

They are specially suited to the production of very high temperatures, such as are needed for burning fire-bricks, but though very efficient in many ways, they are extravagant in fuel unless connected together so as to form a continuous kiln.

Semi-continuous kilns (Fig. 19) are intermediate between the kilns just described and those with a continuous firing. They are more economical in fuel than the former, but less so than the latter, and so are chiefly used where the output is not sufficient for a completely continuous kiln.

Though sometimes regarded as a distinct type of kiln, those working semi-continuously are really incomplete kilns which must be worked as well as the circumstances permit, and completed when trade warrants the erection of additional chambers. If it is probable that the output of the yard will only be small, it is far better to build a small continuous kiln, of the usual length, but only half or one third the usual width, as by this means better results can be obtained. The draughts in them may be chiefly horizontal or down-draught, according to the design of the kiln.

In all the foregoing types, the bricks to be burned are placed in the kiln, arranged in such a manner that the hot gases may circulate among them as freely and evenly as possible. The fires are then lighted and the temperature raised, at first with extreme care and slowness, but later more rapidly, until the goods have been sufficiently heated.

The reason for great caution at first is the necessity for avoiding a rapid evolution of water from the bricks, as, if heated rapidly, the steam formed could not escape, and would crack the bricks, rendering them useless. Even when the greatest care is taken, some bricks are usually damaged by being heated too rapidly at first. Even when the bricks appear to be thoroughly dry they may contain one-seventh of their weight of "combined water," which must be removed before the bricks have reached a temperature much above 500° C.

During the first two or three days the bricks are in the kiln, therefore, the heating must be extremely gentle, and as this necessitates the use of fires which are only allowed to smoulder or smoke and not to burn brightly, the term "smoking" is usually applied to this stage of the firing. This very gentle heating must be continued until the bricks show no signs of giving off steam, this being usually tested by putting a clean, cold poker into the kiln, leaving it there for a short time, and examining it immediately it has been withdrawn. If the bricks are still damp, the steam in the kiln will condense on the cold metal, and will reveal itself in the form of a dew. This test is only a rough one, but it suffices for most brick-makers. Others, especially on the Continent, prefer to continue the heating for a definite number of hours with the kiln at a temperature of, say, 120° C.

It is highly advantageous to have a separate flue for the gases and steam evolved at this stage, and not to pass them into the main flue. The use of such a supplementary flue improves the quality of the bricks, and reduces the amount of fuel required.

As soon as all the moisture has been removed at this temperature, the temperature is raised rather more rapidly, but still steadily, until a dull red heat is obtained. It will then be found that a further evolution of steam often takes place. This is due to the decomposition of the clay, and the liberation of the combined water in it. At this higher temperature the remains of plants which may be contained in the material begin to burn, and time is required for the complete combustion of these and of any carbon which may be in the pores of the bricks. If this stage of the burning is hurried the bricks will be discoloured towards the centre, and will have black cores or hearts.

The temperature is again raised when all the carbonaceous matter has been destroyed, and the heating is continued until the bricks have gained the necessary characteristics, when the kiln is allowed to cool, any openings being closed by slabs of fire-brick, luted up with clay paste, so as to prevent cold air impinging on the hot bricks, and so cracking them. When the kiln is sufficiently cool, the bricks are taken out, and the kiln may then be refilled with fresh ones.

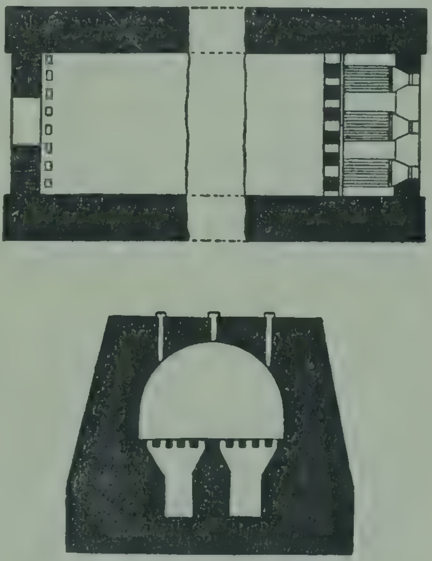


FIG. 19.—Semi-Continuous Kiln.

After the bricks being burned have reached a red heat, the fire gases passing in a single kiln to the chimney are, naturally, very hot, but this heat is wasted in most cases. Many attempts have been made to connect single kilns together by means of flues, so as to utilise this heat as well as that given off by the cooling bricks, but they have not, as a rule, been successful unless the kilns were placed side by side. It was this desire to economise heat which eventually led to the invention of the **continuous kiln**, which consists essentially of a number of single kilns built side by side, with openings in the partition walls.

F. Hoffman went even further than this, and abolished the intervening walls, so that his continuous kiln—which may be regarded as the basis of all modern continuous ones--consisted of an annular space in which the goods were burned (see Figs. 20-22).

The original **Hoffman kiln** is equivalent to a horizontal one of infinite length, the heat being applied to the goods at one end, and passing along them horizontally until the gases are too cold to be of any further use. In practice it is not convenient to have a long narrow kiln, so that the two ends are joined and make a large annular space. It is very important that such a kiln should be sufficiently long, as if the distance travelled by the fire is too short, fuel will be wasted.

On this account it has been customary in recent years to alter the original design of the Hoffman kiln, and to make it either very long with rounded ends (Fig. 20), or to construct it in the form of a series of short tunnels, which turn on each other in a kind of zigzag, so as to produce a kiln, the outside walls of which are almost square in plan (Fig. 21).

In this way much less land, or that of a convenient shape, is used for the construction of the kiln, without reducing its efficiency.

For a kiln containing 14 to 20 chambers, and a total inside chamber length of 220–325 ft. as a minimum, satisfactory results may usually be obtained, but it is necessary to keep all the parts of the kiln in full work if the fullest economy in fuel is to be realised. Hence, when the output of a brickyard is likely to be small, two courses are open to the brick maker: he may construct only half or a quarter of a continuous kiln (thus making a so-called "semi-continuous" kiln), or he may construct a complete kiln with such narrow chambers that the whole can be used, and the chambers widened as the output increases.

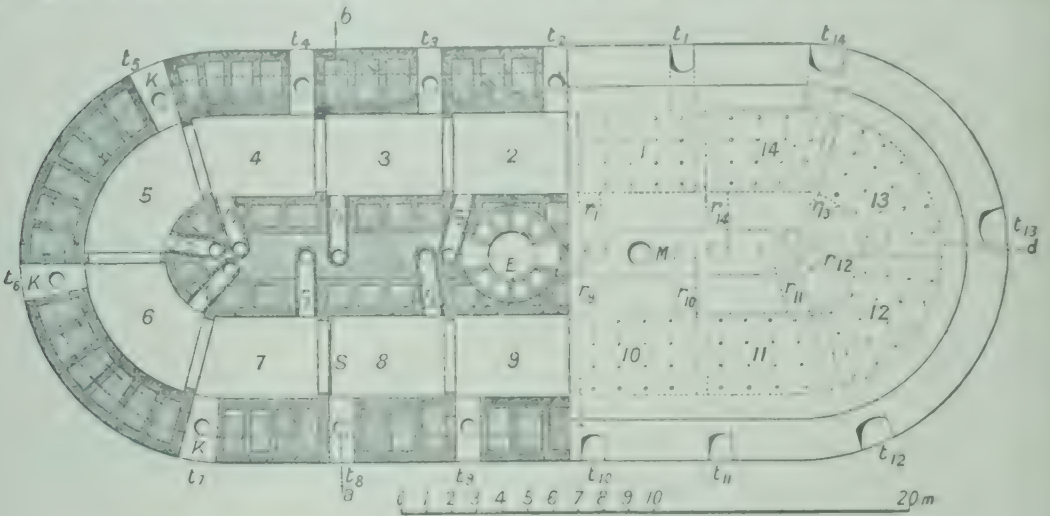


FIG. 20.—Plan of Hoffman Continuous Kiln.

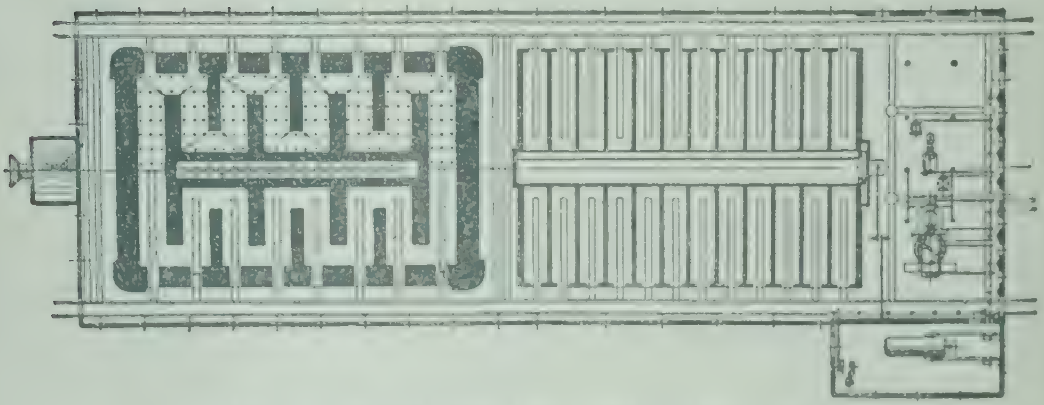


FIG. 21.—Plan of Bührer Continuous Kiln and Drier.

The former is the cheaper of the two, so far as the cost of erection is concerned, but is wasteful in fuel; the latter is much more expensive to erect and alter for enlargement, but the fuel burned is reduced to a minimum.

The method of working a continuous kiln of the simplest type is, briefly, as follows. For convenience it may be assumed that the kiln is in full working order, and contains fourteen chambers. No. 14 is being filled with bricks from the drier or machine house. No. 1 is being "smoked" by a small fire contained in a portable stove, or in a fireplace built in the doorways of this chamber, a partition of iron or of paper separating it from the remainder of the kiln, and making it temporarily into a single kiln. No. 2 is dry Nos. 3 to 6 are being slowly heated without the direct use of fuel, by passing the hot gases from Nos. 7 and 8 (which are being heated by coal) through them. In this way the heat from Nos. 7 and 8, which would, if they were single kilns, be allowed to pass up the chimney and so be wasted, is utilised in the preliminary heating of four other chambers full of bricks, and as the gases pass from one chamber to another they gradually lose their heat, so that by the time No. 3 is reached they are at a temperature of only 150°-200° C. It is then useless to carry them through any more chambers, so they are taken direct to the chimney stack through the main flue. The fuel is supplied through feed holes in the roof of the chambers, and falls into hollow pillars made of bricks, in which it burns. No. 8 is at such a temperature that it constitutes the finishing point of the kiln; the higher numbers are those containing the finished but hot bricks. In order to cool these and so enable them to be taken out of the kiln, the doorway in No. 12 (the last chamber) is opened and air admitted. This air is drawn from No. 12 to No. 9, becoming gradually hotter by reason of its contact with the bricks, so that by the time it reaches No. 8, in which some bricks are being fired, it is hot enough to assist greatly the combustion of the fuel. In this way the heat contained in the cooling bricks is used over again for the heating of a further lot. Taking the chambers in the order given, it will thus be found that the temperature in each gradually rises, Nos. 1 and 2 being at something below 120° C., Nos. 3 to 7 from 120°-900° C., and No. 8 about 1,100° C., or less with some clays. From Nos. 9 to 13 the temperature gradually falls again from 1,000° C. to the temperature at which the bricks are taken out of the kiln—usually about 25° C., or as hot as they can be handled comfortably.

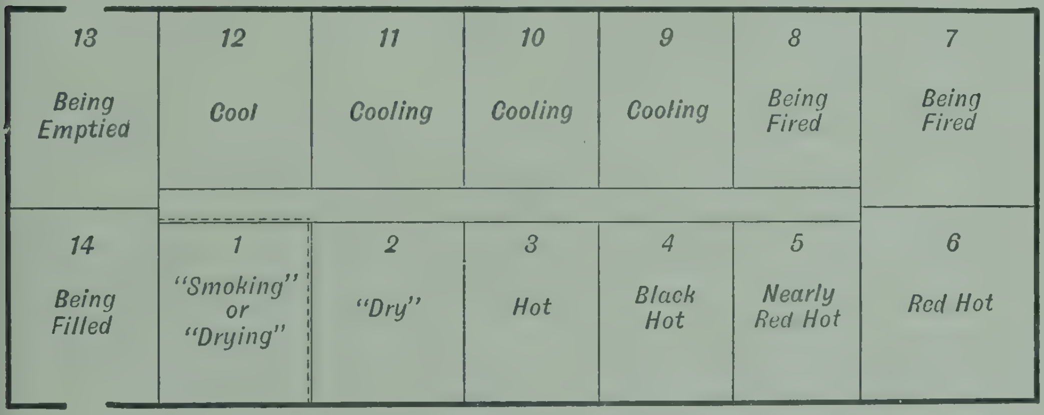


FIG. 22.—Showing State of Goods in Continuous Kiln.

When No. 8 has been heated sufficiently the connection between No. 3 and the chimney is closed and the partition between No. 2 and No. 3 is removed (if it is paper it is simply torn with a poker), so that the hot gases now enter No. 2. Fuel is next fed into No. 6, but no more is added to No. 8, which therefore begins to cool. In No. 1 (which should now be filled with fresh bricks) the "smoking" process is begun so as to drive out the water in the bricks. In this way the whole process of heating is moved on one chamber, and the bricks in No. 12 will now be cool enough to be taken out and it refilled. In this way the action of the kiln is quite continuous so long as there is a sufficient supply of bricks to be burned, as the fire travels forward, usually at the rate of one chamber per day, and the kiln being circular in principle, whatever its apparent form, it acts as though it were of infinite length.

Although a kiln with only fourteen chambers has been described, as this represents the size generally used, the author considers it too short for convenience and prefers a kiln with at least sixteen chambers. The larger the number of chambers (within certain limits) the more satisfactory will be the burning. Some kilns have forty chambers.

Many variations have been made in the design of continuous kilns, though the general principle first applied by Hoffman is continued in each of the newer kilns. The alterations consist chiefly in means used to produce a better colour in the goods by keeping them out of contact with the fuel, and to effect the preliminary drying in the kiln.

The chief variations, therefore, consist in some means of burning the fuel in special fire-boxes and in effecting the drying and smoking by means of warm air derived from the kiln itself instead of from separate fires.

For producing bricks in which the colour is an important consideration the fuel is most conveniently burned in fireplaces built across the kiln between each two chambers, the kiln being usually, though not necessarily, divided by partitions of permanent brickwork. These partitions absorb a certain amount of heat, and so reduce the efficiency of the kiln as a whole, but the small loss from this cause is more than counterbalanced by the improved colour of the goods. There is much divergence of opinion as to the relative values of fire-boxes with solid bottoms and those with grates. Much depends upon the nature of the fuel, and when this will burn on a solid bottom the labour of cleaning the grates is obviously avoided. For other coals, a grate may be essential to good combustion.

In the original Hoffman kiln, the fuel is burned in small shafts left in setting the bricks in the kiln, and corresponding to openings in the top, through which the fuel is fed in small quantities at a time every fifteen or twenty minutes. When fire-boxes or fire-grates are used, however, the fuel is added either from the front of the kiln or through openings in the top and above the grate or fire-box, and larger quantities may be added at a time. The hot gases and flames from the burning coal then rise upwards, but are rapidly drawn horizontally by the draught of the kiln until they circulate throughout the whole width and height of the chamber, the bricks being placed in such a manner that there is an appropriate space around each for it to be properly heated by the gases. If it is desired to produce bricks which are of a specially clear colour, a permanent flash wall may be built alongside the fire-box or grate, so as to force the flame and hot gas upwards to the top of the kiln, where combustion is completed before the goods are reached, and all chances of the flame coming into contact with the bricks are avoided. In this way, a series of down-draught kilns may be worked on the continuous principle, the gases being taken out at the floor of the chamber, instead of at the side as usual. This alteration involves a more complex flue construction, but has certain advantages which need not be detailed here (see Fig. 23).

The use of hot air produced by the kiln itself for the smoking or preliminary warming and drying of the goods has not met with the appreciation it deserves. This is due to a variety of causes, the chief of which is the general attitude of the burners who prefer what, to them, is the simpler method of using stoves or special fires, though the latter are far from economical. The position of the flues used to convey the hot air in certain kilns is also very bad, and has caused this method of economising fuel and labour to fall into disrepute. Not a few designers of continuous kilns have ignorantly placed the hot-air flues in the positions where they are most likely to be influenced by changes in the temperature of the kiln, and by the movement of the masonry, with the result that, after a short time, these flues leak and become practically useless. They should, obviously, be placed where they will be most stable, as a leak of comparatively small dimensions may be impossible to locate or repair, and yet may be fatal to the use of the flue.

The object of using warm air in place of special stoves or fires is two-fold, viz., the economy in fuel effected and (what is usually more important) the absence of white or grey deposits on the bricks due to the condensation on them, whilst in a damp state, of sulphuric acid derived from the burning fuel. When the goods are at a temperature above that of boiling water such condensation cannot occur, and direct heating may then be used, but for raising them to this temperature it is usually desirable to employ air free from products of combustion.

This pure, warm air must not, as a rule, have a temperature above 300° C., and at the commencement of the heating of the freshly set bricks it should be much cooler, though its most suitable temperature cannot be stated definitely, but must be ascertained by experiment, as it differs with different materials, some being more open and so drying more readily.

The warm air used may be obtained from various sources, and can seldom be all obtained from only one. The most obvious part of the kiln from which it may be obtained is the chambers containing the cooling bricks, as by connecting these to the ones containing the freshly set goods, by means of temporary or permanent flues, it is easily possible to draw air of any desired temperature through the latter. The details of the various systems of pipes and flues used for this purpose are too complex to be given here, but it may be stated that permanent flues are usually better so far as the economy of heat is concerned, though they are more liable to leak than the temporary ones, which are generally made of metal.

The heat obtainable from the chambers of cooling bricks is seldom sufficient, and it must, therefore, be supplemented by air heated specially in some other part of the kiln. Many devices have been patented for the supply of this additional air, the two most successful being to construct a series of flues either below the floor or above the arched top of the kiln, and to draw air through these at such a rate that it may gain the desired temperature before it enters the chambers to be warmed. As much of the heat in the brickwork is usually lost by radiation, it will readily be seen that flues arranged in these places will really save a certain amount of heat which would otherwise be lost, so that by no means all the heat thus supplied to the air passing through these flues can be considered as involving an additional consumption of fuel, though there is necessarily a slight increase in the amount of fuel burned in the firing proper when these flues are used. This is so much less than that required in the stoves or special fires that a distinct saving on the whole kiln is effected.

The hot air (from whatever sources) is led through flues to the cold chambers which require to be warmed, and enters them by suitable flues and openings. There is much divergence of opinion as to the best position in which to admit this air, some authorities preferring to allow it to enter at the top and work downwards, whilst others adopt the opposite direction. Personally, the author prefers to use an entirely upward direction for the gases during the smoking, or to dry and warm at least the lower contents of the kiln by means of an up-draught. The reason for this preference is the fact that when the warm air or gases enter at the top of the kiln they gradually become saturated with water removed from the bricks themselves, and at the same time they become cooler, with the result that by the time they reach the lower portion of the kiln they cannot contain all the moisture, and deposit some of it in the form of a dew on to the bricks. The deposition of this water softens the bricks, and, owing to the pressure of the bricks above them, makes them lose their shape. When, on the contrary, the hot air or gas rises in an upward direction, the moisture deposited on the bricks still softens them, but as they have but little weight to bear no change in shape occurs. The upward movement has the additional advantage that must occur from allowing the warm gases to travel in their natural direction, and if they are not overladen with moisture a better draught is produced owing to the reduction of the internal friction of the kiln.

The substitution of a fan for a chimney has not been appreciated to any great extent, because most existing brickworks have chimneys, and their owners do not see that any saving would be effected by the substitution of a fan, especially if they are not working at their full capacity.

In some parts of the Continent, however, and in several instances in this country, the use of a fan has effected a considerable saving in the amount of fuel burned, as it enables the draught of the kiln to be kept constant instead of being affected by climatic conditions, as is invariably the case with a chimney.

The object of a chimney, or fan, is to draw the necessary amount of air through the fuel and gases through the kiln. It is commonly supposed that a chimney does this without cost, whereas a fan requires power to drive it. As a matter of fact, however, a chimney requires the expenditure of a certain amount of fuel, as the gases passing up the chimney must be hot, and this fuel is more than sufficient, in most cases, to drive the fan. In calm weather and under good conditions the fan and chimney, therefore, cost about the same for running expenses, but in rough weather the amount of fuel needed to keep the chimney working is greatly increased, whilst the fan is not affected; and, further, the interest on capital needed for the erection of a chimney or the installation of a fan is much in favour of the latter. For continuous kilns, therefore, a fan should be used when practicable. In single kilns, where no use can be made of the hot gases produced, a fan is not desirable.

In an ordinary kiln of the continuous type it is seldom that the fire travels forward more than 15 ft. per twenty-four hours, and a rate of 1 ft. per hour is considered high. In the Bührer kiln, however, thanks to its enormous relative length and the use of a fan, the fire travels forward at the rate of 8 or even 10 ft. per hour, and the amount of fuel saved is, therefore, considerable. So rapid a rate and so long a kiln could not be obtained when a chimney is used; hence it was only on the introduction of a fan that this method of working became possible. Its success is due to the fact that although the rate of travel of the fire is so rapid this is counterbalanced, so far as its deleterious effects are concerned, by the length of the kiln, for most bricks can be heated very rapidly when once they have reached a dull red heat, provided that they are supplied with sufficient air to burn out the carbonaceous matter in them, and to oxidise the iron compounds. The length of the kiln enables the "waste heat" to be used to warm the goods very effectively without any danger of cracking them. Clays very rich in carbonaceous matter might require a somewhat slower treatment and for these a Bührer type of kiln may be unsuitable.

The great length of the kiln is not apparent in the actual buildings, because it is so designed that it really forms a more compact structure than similar kilns of the ordinary type.

For burning facing bricks, ornamental bricks, terra-cotta, and other similar goods in which the colour and appearance are of very great importance, difficulties have often been experienced when continuous kilns are used, and it has been generally maintained that single down-draught kilns were essential for the production of articles of good colour.

This is quite a mistake, for by arranging a continuous kiln specially for the purpose, goods equally beautiful in appearance to any produced in single kilns may be obtained.

It is quite true that an ordinary continuous kiln will not do for this purpose without alteration, for it is designed chiefly with a view to economical working, but with a suitable arrangement of fires and flues (Fig. 23), especially those for the introduction of warm air and the removal of steam, the best results may be obtained with an expenditure of fuel not more than three-quarters, and frequently less than half, that needed in a single kiln.

The most suitable kiln for this class of work is one in which the draught is partly horizontal and partly downward, fireplaces being provided for burning the fuel, and each chamber separated from the others by permanent partitions, in which, however, damper-controlled openings may be made so that the "waste" gases pass direct from one chamber to another.

The production of a good colour in bricks depends primarily on the material used; but assuming that this is suitable, the most important requirements are (1) that the goods shall not come into contact with the flame or ashes from the fuel; (2) that the goods shall be raised to a temperature above that of boiling water before coming into contact with gases produced by burning fuel; and (3) that the goods shall be supplied with sufficient air at certain stages of the burning, this air supply being capable of accurate regulation.

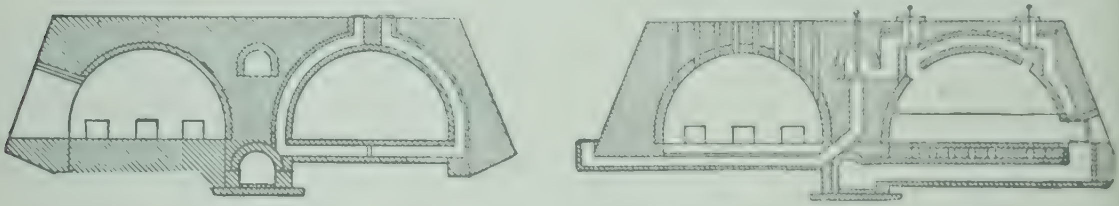


Fig. 23.—Cross Sections of "Staffordshire" Kiln showing Hot-Air Flues.

(*By courtesy of Messrs Dean, Hetherington,, & Co.*)

To fulfil these conditions it is necessary, chiefly, to warm the goods thoroughly with pure air before connecting the chamber containing them to the circuit of the kiln, and the key to the whole position lies, therefore, in the means supplied for the provision of hot air in any quantity, and at any time it may be needed (p. 220).

Tunnel Kilns, in which the bricks are heated on trucks or cars covered with refractory blocks, are gradually replacing the continuous kilns previously used. Unfortunately, such tunnel kilns are more expensive in first cost and upkeep but they enable the workers to work under such better conditions that it is difficult to get skilled workers for the older types of kilns.

Tunnel kilns have the following very important technical advantages:—

(i) Easier filling and unloading under much more comfortable conditions.
(ii) Easier inspection before the goods enter the kiln and after they leave it.
(iii) Easier transport to and from the kiln.
(iv) Much better control of the heating; in some cases the temperature can be controlled automatically.
(v) Much more effective use can be made of pyrometers, draught-gauges, and other control instruments.
(vi) A much more rapid throughput, the goods being burned in three days instead of 14–18 days.

Tunnel kilns with cars do not normally use less fuel than other continuous kilns and they also require power to drive the fans and to move the trucks.

The chief advantages are less labour costs and better control of the heating.

In many common brick-works with existing kilns it would be unprofitable to replace them with tunnel kilns, but when a new works is being erected a tunnel kiln should be carefully considered.

DE-AIRING

When some plastic clay pastes are cut into small rods by forcing them through a series of perforations in a steel disc or by some other method, and these rods are passed into a vacuum and afterwards into a pugmill, the resultant paste is much more plastic and much more "workable" than before. Bars about 2 in. diameter made of such "de-aired" clay can be twisted and tied in knots in a most astonishing manner.

It is commonly supposed that this great increase in workability is due to the extraction of air from the clay paste, but it seems much more probable that it is due to the changes in the water vapour in the paste. Simple re-pugging without removing the air does not have the desired effect.

As a de-airing machine is readily installed without undue interference with the plant as a whole, the use of such machines has been greatly appreciated by many firms using a plastic process.

TESTING BRICKS

Methods for testing bricks are described in British Standard No. 1257 and in Butterworth's "Bricks and Modern Research" (1948).

FUTURE PROGRESS

From 1850 to 1900 the chief progress in brick-making occurred as a result of the introduction of several kinds of machinery and of continuous kilns. These changes were accompanied by a great reduction in the cost of manufacture and an enormous increase in the number of bricks produced.

Since 1900, the introduction of de-airing as a means of increasing the workability of clay-paste, the great increase in the use of the semi-dry or "Fletton" process, and the use of tunnel kilns with cars have made the manufacture of bricks a very different kind of business from what it was prior to about 1900.

Except for the manufacture of the more beautiful kinds of facing bricks, the prospects of brick-yards making less than 10,000,000 bricks a year are meagre, and the few works with huge outputs tend to create a monopoly in common bricks. On the other hand, the carriage on bricks is very costly, so that the transport of bricks over long distances is not economical, and this tends to favour works of moderate size, widely distributed so as to be not more than 30–50 miles from the places where the bricks will be used.

In the past fifty years or so, brick-making has changed from a hand-industry with little machinery into a highly mechanised industry with increasing recognition of the fact that it is fundamentally as much a **chemical** as an engineering one. The large amount of research effected during the last fifty years has very greatly increased our knowledge of the underlying chemical and physical properties of clays and of bricks made from them, and this knowledge is steadily leading to much better technical control of the industry.

Notwithstanding the claims made on behalf of other materials, bricks still remain the cheapest units for many buildings and they are far the most durable.

SECTION LXX

SAND-LIME BRICKS

By Alfred B. Searle
Consulting Technologist

LITERATURE

A. B. Searle.—"Modern Brickmaking." (4th edition.) London, 1953.
—— "Bricks of Non-Plastic Materials." London, 1913.

There are occasional articles in *The British Clayworker* and in *Claycraft*, also a brief, but exhaustive, German literature on this subject.

Patents.—There are numerous patents connected with the manufacture of Sand-Lime Bricks, but most of them are obsolete.

Sand-Lime Bricks.—It has been known for many years that a mixture of slaked lime and sand will dry to a solid mass which hardens very slowly on exposure to the atmosphere, owing to recarbonation of the lime. Partial combination between lime and sand can be induced by submitting an intimate mixture to the action of steam under high pressure. This production of a calcium silicate (or alumino-silicate) cementing together the grains of sand is the essential feature of the process for the manufacture of sand-lime bricks.

The sand should be free from more than 5 per cent. of clay and dark particles, but 1 or 2 per cent. of clay is advantageous.

It was at one time considered desirable that the sand used should contain soluble silica, but this has since been found to be unnecessary. Hence quartz sands are now used extensively, and it is no longer considered that felspar sands containing 5-7 per cent. of soluble silicic acid are the best raw materials for lime-sand bricks.

At least 10 per cent. of the sand should pass a sieve of 150 mesh, and all of it should pass a 20-mesh screen. With increasing percentages of fine sand the compressive strength of the bricks is diminished, whilst their tensile strength is increased. To obtain the best results, however, it is necessary to grade the material very carefully, as the preponderance of many particles of any one size is deleterious.

The lime should be as pure as possible. Magnesia, if present, combines with silica to form a silicate, which is said to have less mechanical strength and to be less resistant to frost. Further tests are necessary on this point, as many excellent bricks have been made using dolomitic lime.

Bricks made with hydraulic limes (see p. 82) are inferior, this form of lime being quite unsuitable, as it does not slake in a suitable manner.

It is advisable to use hydrated or slaked lime, but where unusually wet sand must be employed ground quicklime may be used, though great care is required to avoid accidents.

The lime may be bought in the "quick" or "lump" state and slaked at the brick-works, but it is often more advantageous to purchase hydrated lime as the risk of damage to the bricks from the presence of unslaked particles of quicklime is thereby reduced.

The mixing of the lime and sand may be effected in several ways: (i) The whole of the lime and sand for one batch of bricks may be mixed in a large mill; (ii) A continuous mixing process may be employed though the results are often uncertain; (iii) Part of the sand may be mixed with the lime and the remainder of the sand added later. Each of these methods has its own advantages and the one chosen should depend on an adequate consideration of all the relevant local conditions.

It is important to have as uniform a mixture as possible, with the lime, sand, and water all in suitable proportions. It is usually advisable to have adequate tests made to determine these before erecting a plant.

The mills used for mixing the materials may be of the open edge-runner type with revolving pans, or of the rotating cylindrical type. Illustrations and further particulars of both may be found in "Bricks of Non-Plastic Materials" by A. B. Searle.

The wet mixture of lime and sand is moulded into bricks under a pressure of from 1–1½ tons per square inch. The bricks are then placed on waggons and are run into the hardening chamber where they are submitted, for about eight hours, to steam at 180° C. and 10 atmospheres pressure. The autoclave or hardening chamber is 30–45 ft. long and 5–6 ft. in diameter, and is constructed of boiler plate. The bricks, after leaving the boiler, are then quite ready for the market, but they are usually allowed to remain in stock for a short time.

Specifications for sand-lime bricks of the best quality require an average crushing strength of 2,580 lbs. per square inch with a minimum of 2,560. Second quality bricks should have an average crushing strength of 2,130 lbs. per square inch with a minimum of 1,920. It is interesting to compare these with an ordinary lime-sand mortar (1 lime to 3 sand) which rarely has a crushing strength over 200 lbs. per square inch.

British Standard Specification No. 187 (1942), with Amendment PD 735 (1947), specifies the sizes, strength, and qualities for four classes of bricks, and describes the various tests to be made and the kinds of mortars to be used.

It is most essential that the bricks, when ready for use, should be free from particles of unslaked lime large enough to damage the bricks on exposure to moist air.

Sand-lime bricks are more fragile and in some ways inferior to bricks made of clay, but they are stronger than London stock bricks, and being readily made in districts devoid of clay, they are very useful for most building purposes. Their porosity is similar to that of bricks made of clay, with the exception of engineering bricks, which are purposely made non-absorbent. Sand-lime stone, if well made, possesses great homogeneity and can be easily worked by the mason.

The cost of manufacture of sand-lime bricks is slightly less than that of bricks made of clay, but the difference is not appreciable unless the works are exceptionally well managed.

The manufacture of sand-lime bricks in the United States and in Germany is very extensive. In Great Britain it is small on account of the low prices at which clay-bricks are sold in consequence of competition. In sandy districts where clay is not abundant, sand-lime bricks offer great possibilities, provided that the plant is properly devised and constructed. Most of the failures have been due to ignorance or to a wilful departure from the recognised essentials in order to produce them at a lower rate. When rightly made, sand-lime bricks serve the same purposes as clay building bricks.

BRITISH STANDARD

British Standard Specification No. 187 (1942), with Amendment PD (1947)

SECTION LXXI

TILES AND TERRA-COTTA

BY ALFRED B. SEARLE

LITERATURE

E. BOURRY (translated by A. B. SEARLE).—"Treatise on Ceramic Industries. 1926.
W. J. FURNIVAL.—"Leadless Decorative Tiles, Faïence, and Mosaic." 1904.
E. DOBSON and A. B. SEARLE.—"Bricks and Tiles." 1936.
BRUNO KERL.—"Das Gesammten Tonindustrie." 1907.
A. GRANGER.—"La Céramique Industrielle." 1905.
A. B. SEARLE.—"Modern Tilemaking" (deals only with Roofing Tiles). 1930.
—— "The Clayworker's Handbook." London, 1949.

The chief *periodical publications* dealing with tiles and terra-cotta are: The *Transactions* of the British Ceramic Society, *The British Clayworker, Claycraft,* and the publication of the American Ceramic Society

TILES

TILES are used for three entirely different purposes—(*a*) for roofs and exterior walls; (*b*) for pavements and floors; and (*c*) for interior decorations. In each case a different material is employed, roofing tiles being made of plain clay burned to a moderate degree of hardness, but many of them being somewhat porous, whilst paving tiles must be as hard as possible, and should be completely impervious to water. Decorative tiles are almost invariably glazed, and are really earthenware or porcelain products (see sections on **Earthenware** and **Porcelain**).

Roofing tiles bear a very close resemblance to bricks (p. 213), and are manufactured in a very similar manner, the processes being merely modified to suit the production of thin articles. Such tiles are made of the same clays as bricks, but only the finer varieties are used, as the very coarse particles present in some brick clays would prove detrimental to tiles on account of the thinness of the latter.

No detailed description of the manufacture of roofing tiles is needed here; the reader who requires further information should consult the literature mentioned above.

Paving tiles bear a close resemblance to stoneware (*q.v.*), and to the vitrified or blue bricks of Staffordshire (p. 214), and are made in a similar manner.

They are usually either terra-cotta red, blue, or black in colour, but some buff or yellow tiles are occasionally used for the purposes of decoration. Such tiles are made in a manner similar to bricks or roofing tiles, but require special care in burning; if insufficiently heated they will be soft, and will wear badly, but if overheated they will twist and warp. The chief skill of the paving tile manufacturer is, therefore, employed in the selection of suitable raw materials and in heating them in a suitable manner.

The nature of the raw materials is described under the caption **Stoneware,** but for paving tiles materials of a lower grade and containing more impurities than those employed for the better qualities of stoneware may be used.

In order to obtain highly decorative inlaid patterns, **encaustic tiles** are made. These are produced in moulds with separate divisions. Clay slip or powder of one of the colours to be used is placed in the desired divisions of the mould, and other clay slips or powders of different colours are placed in other divisions, this process being repeated until all the divisions are filled with the appropriate colours and pressed if necessary. After the tile has been removed from the mould and its surface cleaned, the pattern (in colours) will be visible, and on burning will be clearly defined.

As different clays shrink differently it is necessary to use skilfully prepared powders and slips in order that all may have the same shrinkage on drying and burning.

Glazed tiles are used in increasingly large quantities for decorative and hygienic purposes. Most glazed tiles are of an earthenware character and are made in a manner very similar to earthenware (p. 167).

It is possible to glaze red-burning clays such as those of which bricks are made, but the difficulties connected with the use of such clays are usually sufficiently great to render the employment of the mixtures used in earthenware manufacture preferable for glazed tiles.

For hospital use and for some technical purposes, it is necessary to use tiles made of fire-clay and glazed with a hard-fired, leadless glaze, as such tiles are more resistant to acids and variations in temperature than are those made of earthenware and covered with a more fusible, plumbiferous glaze.

Very large tiles (*i.e.*, those measuring more than 12 × 12 in.) are also made of the same materials, further particulars of which are described under "Glazed Bricks" (p. 214), or "Sanitary Ware" (p. 208).

FIG. 1.—Tiles in Sagger.
(*After E. Bourry.*)

The manufacture of very large slabs of glazed ware is accompanied by many difficulties, the chief of which are due to the tendency of clay to twist or warp when heated in the kilns. For this reason it is essential that such slabs should not be too thin to resist this twisting action. Unglazed slabs may sometimes be kept flat by weighting them when in the kiln, but as nothing must be allowed to touch a glazed surface when the goods are being fired, this method cannot be applied to glazed slabs or large glazed tiles.

ARCHITECTURAL TERRA-COTTA

Until about 1930 there was an enormous demand for large masses of burned clay—both plain and ornamental—for the exteriors of large and semi-public buildings, particularly in industrial centres. In some localities the natural colour of the burned clay is preferred, and **terra-cotta** is therefore used; but in other places a light coloured or almost white glazed surface is desired, and for this purpose what is known as **glazed terra-cotta** is employed.[1]

Ordinary terra-cotta is made of any clay which has a sufficiently uniform and pleasing colour when burned. The better kind of brick and roofing tile clays (p. 145) are, therefore, used in its manufacture.

Ordinary terra-cotta blocks are, in fact, exceedingly like large bricks, and are made in a very similar manner, the chief differences in manufacture being the moulding by hand, or the direct carving or modelling of the block from a mass of clay paste, instead of using mechanical means for its production, and the special precautions required in order to prevent irregular shrinkage, twisting, or a blotched appearance of the blocks. These details are, however, outside the scope of the present work, and the reader who requires further information must consult an expert on the subject or read some of the works mentioned under the caption Literature on pp. 161, 213, and 241.

Glazed terra-cotta must usually be made of a more refractory clay than that used for unglazed terra-cotta, as the only glazes applicable to the latter are seldom able to withstand the action of the British climate, especially the atmosphere in large towns with a manufacturing interest. Hence the general use of glazed terra-cotta made of fire-clay or covered with a hard fired glaze similar to that used for sanitary ware, but of a less glossy character.

---

[1] This demand will probably recur when the building trade has revived sufficiently after the Second World War (1939–45).

For exterior work, a highly lustrous glaze would not be pleasant, so that the glazes actually used are purposely made deficient in fusible matter or fluxes, and in this way they produce a semi-opaque, dull, or even matt glaze. The essential constituent of these glazes is felspathic material, the fusibility of which is modified so as to suit the requirements of the case by the addition of various fluxes such as whiting, or of opacifying and shrinkage correctives such as clay and flint.

Hollow partition blocks are a form of architectural terra-cotta which has met with very extensive application for many years. They are chiefly used for floors, for the filling of wall spaces in buildings of steel or concrete, and are economical in erection as well as possessing other advantages such as lightness combined with highly sound-proof properties. Such hollow partition blocks are made by expressing the clay paste through a special die in a manner similar to the manufacture of sausage, the hollow portions being formed by cores inserted in the mouth-piece and the blocks being cut to a suitable length. In order that the walls may be sufficiently soft and tenacious for nails to be driven into them, the clay is usually mixed with a considerable proportion of fine sawdust; this burns away in the kiln, leaving a porous material which is very light and is admirably suited for inside work (see Wire-cut Process, p. 208).

Flooring blocks of terra-cotta are extensively used in concrete construction. They closely resemble the hollow partition blocks just mentioned, and are made in a similar manner. Their shape varies greatly according to the ideas of the architect or engineer using them, some preferring rectangular blocks whilst others prefer pipes of triangular or half-round section. As the terra-cotta is buried in concrete its appearance is of small importance, and so long as it possesses the required strength it is immaterial of what clay it is made. In the majority of cases, however, such flooring blocks are made of plastic red-burning clay with or without the addition of sawdust.

SECTION LXXII

FURNACE LININGS AND OTHER REFRACTORY MATERIALS

By Alfred B. Searle
Consulting Technologist

LITERATURE

A. B. Searle.—"British Clays, Shales, and Sands." 1912.
—— "Modern Brickmaking." 1931.
—— "The Clayworker's Handbook." 1949.
—— "Refractory Materials: their Manufacture and Use." 1940.
E. Bourry (translated by A. B. Searle).—"Treatise on Ceramic Industries." 1926.
C. Bischof.—"Feuerfesten Tone." 1904.
F. Wernicke.—"Fabrikation der feuerfesten Steine." 1921.
Bruno Kerl.—"Handbuch der gesammten Tonindustrie." 1907.
H. Schnurpfeil.—"Tonindustrie im Glashüttenbetriebe." 1908.
H. Seger.—"Gesammelte Schriften." 1908.
American refractory clays are described in "Clays, their Occurrence and Properties," by H. Ries.
"Steel Plant Refractories" by J. H. Chesters can be particularly recommended to metallurgists.
For a small elementary book, see "Refractories for Furnaces, Kilns, Retorts, etc." by A. B. Searle. 1948.

The Journal of the Society of Chemical Industry, *The British Clayworker*, *The Refractories Journal*, *Ceramics*, *The Journal of Gas Lighting*, and the *Gas World* contain the most recent publications on refractory materials with abstracts from the chief foreign books and journals. The *Transactions* of the English and American Ceramic Societies also contain frequent papers on the subject.

The British Ceramic Research Association (Penkhull Stoke-on-Trent) publishes a series, of Bulletins which contain the results of a large amount of research on refractory materials (for use of its members only).

Patents.—There are many patents relating to refractory materials and inventors of new processes or materials should be careful to ascertain that they do not infringe existing patents.

Raw Materials.—The essential characteristic of any refractory material is that it must withstand the action of high temperatures for as long a time as the purposes for which it is used may render necessary.

Bricks are not termed **graded** fire-bricks if they begin to melt at a temperature lower than 1,580° C.

In practice, however, other considerations are also to be taken into account. Thus, a fire-brick may, of itself, be able to resist the highest temperature to which it is exposed, but it may be less valuable, for some purposes, because it is unable to resist the cutting action of the furnace gases or slag like another fire-brick which is less resistant to a high temperature alone. For this reason many fire-bricks are in use at the present time which are not distinguished for their remarkable refractoriness when heated in a clean atmosphere, but which do possess an exceptional resistance to the actual conditions which prevail in the furnaces or other structures in which they are employed.

One of the first considerations in selecting a fire-brick or other refractory article should therefore consist in ascertaining precisely what are the conditions under which the brick or other article will be used, and the various forces to which it is desired it shall be resistant.

Thus, a metallurgical furnace will usually involve the production of a considerable amount of slag of a basic character, and this will rapidly attack any purely siliceous lining, but will have a far smaller action on a lining made of a highly aluminous clay. If the nature of the operation involves the production of acid or neutral products, on the contrary, a more siliceous clay (which is cheaper), or even a comparatively pure silica or ganister may be used. In the construction of flues and boiler settings, on the other hand, the chief difficulty is to find a material which will resist the cutting action of the dust in the gases and the reducing action of the gases themselves. For such purposes it is therefore more important to have a close-surfaced brick of a hard and strong nature rather than a soft and porous surface made of a material somewhat more resistant to the action of heat alone.

The selection of a refractory material must therefore depend on the purposes for which it is to be used, and in cases of doubt it is wise to obtain expert advice upon the subject, or at least to inform the manufacturers of the bricks of the purposes for which they are intended. Thus, coke ovens and cement kilns are lined with bricks rich in alumina, glass tanks are made of siliceous clays, and basic furnaces must be lined, in the lower part, with basic bricks.

The raw materials used in the manufacture of refractory goods such as fire-bricks, gas retorts, glass makers' pots, furnace linings and crucibles, etc., must necessarily possess a sufficient resistance to heat to enable them to be used for the desired purpose. It is, in fact, generally recognised that no material which shows distinct signs of fusing when heated to a temperature of 1,580° C. should be regarded as refractory, and should therefore be excluded from the mixture of which refractory goods are made. The one exception to this is when the goods are made of non-plastic material and a binding agent is necessary to unite the particles together: this binding agent cannot as a rule be refractory, as its purpose is opposed to the properties possessed by refractory substances. The ideal binding agent is, however, one which is affected by heat until in a state when it binds the particles together, but after this it combines with the particles themselves in such a manner that the action of heat upon it is no longer observable.

The basis of all refractory articles is either fire-clay, one of the various forms of relatively pure silica which occur in nature, or an infusible oxide such as alumina, lime, or magnesia. The fire-clays occur chiefly in the Coal Measures, in intimate association with the coal seams, but those in some districts, such as around Stourbridge, in central Yorkshire and in the West of Scotland, are superior to most of the fire clays found in other localities. As already remarked, however, it is not necessarily the most infusible clays which are the most resistant under given technical conditions. Fire-clays are distinguished by their relative freedom from lime, magnesia, potash, soda compounds and iron, though they usually contain small proportions of each of these substances.

No direct connection has yet been found between the composition of a clay and its resistance to heat, but this may be due to the difficulties experienced in accurately measuring the effect of heat rather than to the absence of such relationship. Several investigators have found an approximate connection between the composition of the purer fire-clays and their softening temperatures, but the difficulty of ascertaining the temperature at which a fire-clay begins to melt and the ease with which erroneous conclusions may be drawn on account of the complexity of the clays and their low conductivity of heat, prevent any accurate relationship being found at the present time. There is, in fact, considerable scope for investigation of this relationship, but the research would have to be taken up by men sufficiently well acquainted with the difficulties and peculiarities of the problem, or erroneous conclusions would almost certainly be drawn. For instance, it is commonly understood that clays do not possess a single melting point, but fuse over a range of temperature, instead of sharply, as do substances of definite chemical composition; it must be remembered however that the conductivity of clay is so low that an abnormally long time is required for the whole of the mass to attain to a given temperature, it will readily be understood that the apparent range of fusion is entirely due to the low conductivity of the clay. The more rapid fusion of very small pieces of clay rather confirms this postulate, though the difficulty of avoiding irregularities in composition, when very small fragments are examined, increases the difficulty of drawing accurate conclusions.

Whilst, therefore, the composition of a fire-clay as revealed by analysis will not necessarily indicate its refractoriness, it may be generally understood that all the more refractory clays do not contain more than 3 per cent. of basic oxides such as lime, magnesia, potash, and soda (the last two being commonly considered together under the term **alkalis**). Iron compounds behave peculiarly in fire clays but it is seldom that more than 2 per cent.—calculated as ferric oxide—is permissible, and a much smaller proportion is generally more desirable.

In consequence of the small proportion of iron present (and that usually in the form of pyrites), fire clays do not burn red as do most building bricks, but produce goods of a pale buff or cream colour, their appearance being often spoiled by small black spots due to the reaction of the ferrous silicate, derived from the pyrites, on the clay.

These spots are not produced unless the clay has been heated to a somewhat high temperature and some makers of fire-bricks therefore burn their goods at temperatures not exceeding [illegible] C.; users are, however, gradually realising that the black spots which disfigure the surface of bricks burned at higher temperatures are really an index of the temperatures reached in the kiln and are thus, indirectly, a testimonial to the refractoriness of the bricks. This is particularly noticeable in the case of the Glenboig bricks which are among the most heat-resisting bricks known.

Instead of an analysis, it is preferable for the purchaser of fire-clays or refractory goods to know the results of the action of heat on the material; this usually takes the form of a statement as to the "softening point" (often, but inaccurately, termed the "fusing point" or "melting point"). This is determined by making the material into the shape of a small tetrahedron whose height is five times its base and heating it slowly in a suitable furnace. The temperature at which the apex of the tetrahedron bends over and touches the base is regarded as the softening point.

To obtain the best results it is necessary to standardise the shape and size of the samples and, instead of measuring the temperature, to compare the behaviour of the sample with that of Seger cones and to report the softening point in terms of Seger cones. The Institute of Gas Engineers, in their official specification, adopt a somewhat different definition, inasmuch as they regard the softening point as that at which the first signs of fusion can be observed in the sample, especially by a rounding of the edges. There is no very definite relationship between this and the bending just described, though the latter usually occurs at a temperature about 60° C. higher than the former with the purer fire-clays.

Other tests, which reproduce the conditions likely to be experienced in actual use, are very important. Among these, are the behaviour of the articles—

(*a*) when heated under a steady pressure under a rising temperature or under a rising pressure at a maintained temperature (**refractoriness under load test**),

(*b*) their behaviour when rapidly cooled from a high temperature (spalling test),

(*c*) their resistance to a rotating abrasive disc, and

(*d*) their resistance when a small mass is placed on them and heated until it becomes quite fluid.

Fire-clay bricks and similar articles are made of a paste prepared by mixing the finely ground fire-clay with powdered calcined fire-clay and water. The grinding is accomplished in edge-runner mills similar to those used for building bricks (p. 218), and the mixing is usually effected in open mixers (p. 219) or even in pug mills (p. 221), the vertical pattern being generally preferred to the horizontal ones used for ordinary bricks.

The calcined clay or **grog** is used to keep the shrinkage of the brick as low as possible, and also to give an open texture so that the fire-bricks will resist the disruptive action which sudden changes in temperature have on fine-textured masses.

The use of grog consisting of particles of suitable sizes is very important.

Fire-bricks and blocks are moulded in wooden frames, the bottom of the mould being formed by the table on which the frame rests, and the method used is precisely similar to slop moulding (p. 220) as used in some localities for ordinary building bricks.

In recent years, fire-clay bricks made by the stiff-plastic process (p. 222), or by very lightly pressing wire-cut bricks (p. 222), have been preferred because of their more accurate shape. This accuracy is important because the thinner the joints between the bricks the more resistant will they be to attack by slag. For this reason, some brick manufacturers grind their bricks accurately to shape with an abrasive wheel.

The fire-bricks or blocks are dried on steam-heated floors in a similar manner to plastic made building bricks, but if the blocks are very large it is necessary to exercise unusual care in drying them.

Where the output is sufficiently large, fire-bricks may be dried in tunnel or corridor driers (p. 226), which are more economical in labour and fuel but do not afford the same facilities for inspection during drying.

It is exceedingly difficult to make large numbers of blocks measuring more than 2 ft. × 2 ft. × 2 ft. and above this size the cost (largely due to risk and difficulty in manufacture) soon grows out of proportion to the size of the blocks produced. Large hollow blocks are somewhat easier to produce than solid ones, as they dry more uniformly and regularly and are less subject to cracking.

Gas retorts are "built up" around an internal core, which is lifted as the work proceeds. They are built vertically, and great care and skill are needed to join the fresh clay on to the old, as the construction of a single retort occupies several days, and each length of 2 ft. or so must be allowed to stiffen before the next portion can be added.

Glassmakers' pots are made similarly to gas retorts and like them require several weeks to dry. The drying cannot be hurried without serious risk of damaging the goods by the internal strains induced by irregular drying, and many precautions have to be taken, particularly during the earlier stages, to secure such large articles being dried uniformly.

Considerable improvements have been made in methods of drying retorts and glass pots during the past few years, but even with these the removal of the water is a slow and anxious process.

Crucibles are made from a paste of similar composition to that used for fire-bricks, moulded in either hand-operated moulds or in a press similar to that used for pottery.

For many purposes the addition of carbon (in the form of coke, coal dust, plumbago or graphite) is made to increase the thermal endurance of the crucible and also to prevent undue oxidation of the contents.

For experimental and certain industrial purposes, crucibles are also made of zirconia and other highly refractory oxides, using hydrolysed ethyl silicate as a binding agent (see p. 251).

The **burning** of fire-clay goods must usually be effected at a much higher temperature than that necessary for common bricks or terra-cotta. Some fire-bricks are burned at as low a temperature as 1,180° C., but for all except the lower grades of fire-bricks a higher temperature is desirable. The precise temperature must depend partly on the clay and partly on the purpose for which the goods are to be used, the wisest plan being to heat the goods in the kilns to such a temperature so that they will not contract appreciably when in use.

This means that the manufacturer must usually heat the goods to a higher temperature than that they will experience when used. Unless this is done, the goods will shrink or contract, and this will tend to loosen the bricks if used for a furnace lining or to cause cracks in a glass pot, retort or other large vessel.

The **kilns** employed for refractory goods are usually single kilns of the horizontal ("Newcastle") or down-draught type (pp. 229–236), as these permit of the very high temperatures being attained with comparative ease.

Because the use of single kilns is very far from economical in fuel, chamber kilns on the continuous principle devised by Hoffman (p. 232) are being increasingly used in the larger works, as they save half or even three-quarters of the fuel required by the single kilns.

Tunnel kilns with cars are also used extensively; they make the handling of the bricks much easier and the control of the temperature and of the burning much more accurate.

Bauxite bricks are made in a similar manner, but as the bauxite contains a large proportion of combined water it must be calcined before use. The calcined bauxite is then crushed to a rough powder, mixed with sufficient clay to bind it, and is then made into bricks. The dried bricks are afterwards burned in kilns at a temperature dependent on that in the users' furnaces, but seldom below 1,400° C.

Bricks made of mixtures of fire-clay and bauxite are much more refractory than those made of fire clay alone. If the proportion of added bauxite is suitable, the resulting bricks are composed almost wholly of **mullite** ($3Al_2O_3$. $2SiO_2$) and have a refractoriness equal to that of Seger Cones 35–38 (1,770–1,850° C.). They have a very low coefficient of expansion and little tendency to spall.

The term **sillimanite bricks** is often applied to bricks made chiefly of calcined kyanite (Al_2O_3. SiO_2.) which on heating in the kilns forms mullite (*supra*).

Bricks made of fused alumina are used in the construction of glass-melting tanks. They have a very high refractoriness, a great resistance to alkalis and slags, and a low expansion. They are too expensive for use in furnaces not working at highest commercial temperatures.

Silica bricks are made of **ganister** or other convenient form of silica rock or sand; the method of manufacture is, however, quite different from that used in making bricks of fire-clay. The material is crushed to powder (unless it occurs in the form of a sand, as in some parts of Wales), and is then mixed with a small quantity of milk of lime, the quantity added being such as to introduce not more than 2 per cent. additional lime into the bricks.[1] The silica, lime, and water [2] are mixed together in a tempering mill, which resembles a mortar mill but is more strongly constructed, and by this means a sandy paste is produced. This paste is almost devoid of plasticity, and requires to be handled with some skill by the men engaged in moulding the bricks.

The bricks may be moulded by hand, in wooden or metal moulds, the material being compressed by means of a small plunger operated by a foot-treadle.

For many years it was found impracticable to shape silica bricks in presses (p. 226), but this method is now largely used as it is cheaper, quicker, and can be made to produce more resistant bricks.

Owing to the absence of plasticity, silica bricks may be dried quite rapidly on steam-heated floors (p. 226), or in a tunnel drier (p. 227), and are then placed in a kiln to be burned. The kilns used for this purpose are the same as those used for fire-clay (p. 247), but a sufficiently high temperature is essential, silica bricks seldom being burned at a temperature below 1,400° C., and one of 1,500° C. being generally preferable.

Silica bricks do not contract is use; on the contrary, they expand (owing to the conversion of the silica into cristobalite and tridymite), and it is, therefore, necessary to heat them in the kilns for a sufficient time, and at a sufficiently high temperature to prevent any further appreciable amount of contraction occurring when the bricks are in use. The remarks made on p. 247 with regard to the finishing temperature of fire-clay bricks applies with equal force to those made of silica.

During the burning, the lime added to the silica, together with any lime, magnesia, and "alkalis," present in the material, combine with the silica and form fusible silicates which bind the less fusible particles into a strong mass.

Only certain quartzites can be used for the manufacture of silica bricks: others split up too readily when heated. The physical properties of suitable forms of quartzite are, therefore, more important than the results of a chemical analysis.

Basic bricks are made by calcining magnesite to the point of incipient fusion, and mixing it with lightly calcined (or caustic) magnesia, forming it into bricks in a manner similar to that described for silica—but without using any lime—and burning in similar kilns and at a similar temperature. Dolomite bricks are cheaper, but not quite so refractory.

Magnesia bricks are chiefly used in furnaces where the slags are strongly basic, and would rapidly corrode linings made of silica or fire-clay, as in the Thomas & Gilchrist process for steel-making.

Dolomite bricks disintegrate on exposure to moist air. To reduce this risk, an addition of a suitable silica compound is now made, serpentine, talc, or steatite being chiefly used. This forms a non-disintegrating silicate with the lime and renders it harmless.

Magnesite spinel bricks are made from a calcined mixture of burned magnesite and bauxite or disapore and are very highly refractory and resistant to slags.

---

[1] It is important to use a properly graded material, *e.g.*, one leaving a residue of 60 per cent. on a British Standard 25-mesh sieve, 20 per cent. on a 72-mesh sieve, 10 per cent. on a 150-mesh sieve, and passing about 10 per cent. through a 150-mesh sieve. Precautions must be taken to prevent the workers contracting silicosis.

[2] About 7 per cent. of water is usually required. The proportion should be carefully controlled or the bricks will vary in size.

Neutral bricks are sometimes preferred to those which are definitely basic (as magnesite bricks), or acid (as silica or fire-clay bricks). They are usually made of **bauxite**—a form of alumina which may contain a considerable proportion of iron—or of chrome iron ore (**chromite**). The **chromite bricks** are made in a similar manner to silica bricks, various bonds being used instead of lime, and clay being the most generally successful.

Chrome-magnesite bricks are made of magnesite or dolomitic lime and chrome ore. They have a greater refractoriness-under-load than chromite bricks and a greater resistance to spalling. When in contact with iron oxide or iron-bearing slags they swell and tend to disintegrate. This disadvantage may be reduced by including a little talc in the mixture used for making the bricks.

Zirconia and **zircon** bricks are highly refractory but have caused disappointment to some users; they are very expensive.[1]

Carbon blocks are being increasingly used in some forms of steel-furnaces on account of their non-absorbent and slag-resisting properties. Those made in recent years are much superior in quality to carbon blocks made many years ago.

Carbon is completely resistant to slags and molten metals; it is one of the most highly refractory materials and its strength is not changed by heat alone. In the presence of air it burns away, but there are parts of some furnaces where the loss from this cause is not serious. The prospects of a greatly increased use of such blocks are worth noting.

Insulating bricks.—During recent years much use has been made of highly porous insulating bricks which reduce the amount of heat lost by radiation from the walls of furnaces and kilns. Such bricks may be made of Kieselguhr and fine clay or of a mixture of fire-clay and sawdust; the sawdust burns away and leaves a highly porous product.

Silicon carbide bricks, blocks, etc., are valued for their high refractoriness coupled with their great thermal conductivity; this enables the material to be used for crucibles and other heat-resisting ware. Various articles made from silicon carbide are also used for "kiln furniture," *i.e.*, for supporting pottery and other articles whilst being fired in the kiln.

Silicon carbide is more commonly known by its registered trade name **Carborundum**, the proprietory rights of which are owned by Carborundum Co. Ltd.

Silicon carbide is made by fusing petroleum residue or similar form of carbon with fine quartz sand in an electric furnace and separating the resultant crystals (see pp. 400–403).

Refractory Cements

Great use has been made during the past 25–30 years of stiff pastes composed of refractory materials. Such pastes may be made of grog (p. 173), silica rock, calcined magnesite, etc., mixed with a solution of water glass or with fire-clay and water. The consistency should be such that the paste can be applied readily with a trowel and spread to the desired shape. Such pastes are used for patching furnaces, fireplaces, etc., and for the construction of monolithic linings for furnaces.

Dry Refractory Cements, of a similar composition, are also available and are preferred by some users. They require to be mixed with water before use.

Refractory Concrete is made of high alumina cement and grog or silica rock; as its name implies, it can be used in the same manner as concrete, which, in furnaces and other situations where the high temperatures attained, would destroy ordinary concrete.

Most refractory cements are sold under branded names.

There is much difference of opinion as to the relative values of different refractory materials for furnace linings, but the scientific evidence available is exceedingly small. In some instances there is no choice. It is, of course, impossible to use a siliceous or even a fire-clay lining for furnaces employed in the Thomas & Gilchrist process of steel-making—but in many cases where a choice does exist it is often very difficult to decide which material is the most suitable for the purpose.

As a general rule, the best fire-clays are more resistant both to heat and to corrosion than are bricks made of silica, but silica bricks are often better than those made of inferior or "second quality" fire-clay. Silica bricks are also more capable of resisting pressure at a high temperature than are some of the close textured fire-clay bricks now on the market, and are therefore better adapted for some metallurgical furnaces. On the other hand, fire-bricks of good quality and suitable texture will not spall or break up so readily as silica bricks when exposed to sudden changes in temperature.

---

[1] Great improvements in bricks and other articles made of non-plastic refractory materials have resulted from the use of ethyl silicate and similar compounds as bonds.

By using a non-shrinking refractory aggregate with such a bond, articles of highly accurate size and shape can be made much more rapidly than when clay is used, but they are also much more expensive.

Various attempts have been made to devise standards for fire-bricks of different kinds, but none of these can be regarded as satisfactory, and for the present, at any rate, experience must be regarded as the best guide in the selection of refractory materials. The regular testing of refractory bricks is very important, and if the results of these tests are treated statistically they increase greatly in value.

For this purpose, the chief tests are:

(i) Refractoriness under load;
(ii) Resistance to thermal shock;
(iii) Resistance to corrosion by slags;
(iv) The specific gravity and volume weight (chiefly in the case of silica bricks).
(v) Shrinkage or expansion on reheating at 1400° C.

The routine chemical analysis of fire-bricks is chiefly of value in suggesting the causes of lack of durability due to an excess of alkalis in clays or silica rocks and, occasionally, to other impurities.

It should be observed that what is quite suitable for one part of a furnace is not necessarily suited to another, and it is the practice among the better furnace builders to use different kinds of bricks in the various parts of the structure. Thus, the outside of many furnaces may usually be faced with good building bricks, which are more weather-resisting than fire-bricks, and the upper part of the furnace may be built of a cheaper fire-brick than those used for the hearth or the parts which come into intimate contact with the hot metal or slags. In some cases the furnace is lined with dolomite and tar, or with ground ganister, rammed into position like concrete, this giving a more satisfactory result than a fire-brick lining, and one which can be more cheaply renewed or patched.

FUTURE PROGRESS

Prior to 1900 fire-bricks were chiefly made of fire-clay in the simplest possible manner, though silica bricks were used for parts of some steel-making furnaces.

Fire-clay bricks shrink during manufacture and also in use, and at the period mentioned it was very difficult to make them accurately to size. The first great improvement was made by replacing most of the raw clay by grog (*i.e.*, burned fire-clay) which was crushed and reduced to particles of suitable sizes. These were then mixed with raw fire-clay and made into bricks which retained their shape and size much more effectively than bricks made wholly of raw clay. This use of grog was much more extensive in Germany than in Britain. It was further developed by an increasing use of non-plastic refractory oxides which were bonded with clay or some form of organic silica (see p. 251).

At the commencement of the war in 1914. British manufacturers of refractory materials were making slow progress and had only just begun to realise the extraordinary success obtained by the German manufacturers in similar materials. When the German supplies were cut off, and the demand for refractory materials was increased very largely, the matter was taken up by the Ministry of Munitions and by numerous committees, with the result that manufacturers determined to act in greater unison than heretofore, and considerable progress was made.

Since then, with the aid of a large amount of effective, fundamental research, numerous lectures and classes dealing with the subject, and a remarkable amount of private enterprise, the quality of almost all kinds of refractory materials have greatly improved.

Close adhesion to specifications for refractoriness under load, shrinkage on reheating, specific gravity and volume-weight, have resulted in bricks of much greater durability and better quality. The best fire-bricks are of better shape and vary in size much less than those formerly made. Some firms grind their bricks accurately to the desired sizes.

Most manufacturers take a great interest in still further improving their products.

In order that this progress may continue it is necessary that the manufacturers should be properly organised and that they should be provided with sufficient capital to enable them to carry out the necessary, yet highly complex, researches. The existence of many small firms with antiquated equipment limits the amount of progress which can be made in this branch of industry.

The future of the great metallurgical industries is so closely bound to the manufacture of refractory materials that there is ample scope for much further development and for still more advanced research.

The production and properties of sintered and fused refractory oxides offers important prospects of advancement and methods.

New products of greater refractoriness (enabling metals and alloys of high melting points to be produced more readily) are being increasingly manufactured. The so-called rare oxides are chiefly used for this purpose (see **crucibles**). In these products the chief ingredient is a highly refractory oxide which is mixed with a less refractory bonding agent or a bond may be formed by heating the crucible or other article to a sufficiently high temperature. Such articles must usually be of moderately small size, but they can be made of great stability under the most trying conditions of heating and cooling and enable much higher temperatures to be used industrially than was thought possible 30–40 years ago.

SECTION LXXIII

GLASS

By Alfred B. Searle

Revised by Marcus Francis

LITERATURE

L. M. Angus-Butterworth.—"The Manufacture of Glass." Pitman, London, 1948.
——, "The Manufacture of Glass." Pitman, London. pp. 286.
R. Charan.—"Handbook of Glass Technology." (2nd edition, pp. 440.) Privately published, Benares, 1946.
J. Home Dickson.—"A Handbook for Students and Technicians." Hutchinson's Scientific and Technical Publications, London, 1951. pp. 300.
E. Dixon.—"A Survey of the Indian Glass Industry." 1936.
—— "Flat Glass and Prelated Glass Products." U.S.A. Tariff Survey, 1937.
—— "Glass Factory Directory." U.S.A. (natl. Glass Budget, Pittsburgh), yearly.
Geo. S. Duncan.—"Directory of the British Glass Industry." 1934.
Henry Eccles.—"Glass Working for Luminous Tubes." 1937.
C. R. Fettke.—"Glass Manufacture and the Glass Sand Industry of Pennsylvania." 1948.
F. Friedrichs.—"Das Glas im Chemischen Laboratorium." Rheydt Rhld., 1951.
E. J. Gooding and E. Meigh.—"Glass and W. E. S. Turner, 1915–1951." Society of Glass Technology, Sheffield, 1951. pp. 140.
Guilleaume Jauneau.—"Modern Glass." 1931.
—— "Report of Indian Tariff Board on the Glass Industry." 1932.
H. Jebsen-Marwedel.—"Tafelglas." Girardet. Essen, 1951.
J. T. Littleton and G. W. Morey.—"The Electrical Properties of Glass." 1933.
P. Marson.—"Glass and Glass Manufacture." Pitman, London, 1949. (4th edition, pp. 155.)
W. Morey.—"The Properties of Glass." 1938.
M. C. Nokes.—"Modern Glass Working and Laboratory Technique." 1937.
W. L. Patrick *et al.*—"German Glass Industry." (Tech. and Industrial Intelligence Reports No. 3). Mapleton House, New York, 1947. pp. 155.
C. J. Peddle.—"Defects in Glass." 1927.
J. Perry.—"Glass Industry." (America at Work). Longmans, Green & Co., New York, 1945. pp. 128.
C. J. Phillips.—"Glass, The Miracle Maker." Pitman, London, 1948. pp. 447.
R. Schmidt.—"Der Praktische Glasschmelzer." Dresden, 1951.
S. R. Scholes.—"Modern Glass Practice." 1941.
S. R. Scoles (translated from French).—"Glass Tank Furnaces." 1937.
L. Springer *et alii.*—"Lehrbuch der Glastechnik." Dresden (Springer), 1949/50.
J. E. Stanworth.—"Physical Properties of Glass." Oxford, 1950.
Verney Stott.—"Volumetric Glassware." 1928.
W. A. Thorpe.—"English Glass." 1935.
W. E. S. Turner (ed.).—"The Constitution of Glass (Symposium)." 1927.
F. Twyman.—"Prism and Lens Making." 1942.
Sidney Waugh.—"Art of Glass-making." 1937.
W. A. Weyl.—"Coloured Glasses." (Monographs in Glass Technology). Society of Glass Technology, Sheffield, 1951. pp. 557.
C. W. Whall.—"Stained Glass Work." Pitman, London, 1948.
D. O. Woodbury.—"The Glass Giant (Lens) of Palomar." 1940.

Glasses are bodies which have been cooled somewhat rapidly from a high temperature at which they existed in the molten state, so that on cooling they remain amorphous in form, and partake of the nature of "solid fluids." That is to say they behave in many respects like a fluid though apparently solid. For some purposes it is convenient to regard glasses as fluids of remarkably high viscosity, so that they flow with extreme slowness and in many ways are indistinguishable from solids. The fact must not be overlooked that the glassy state is purely physical, and may have little relationship (if any) to the composition of the glasses, though commercially valuable glasses show striking analogies in composition. Hence, the term glass is now largely confined to a group of silicates of well-known (ultimate) composition.

Most of the glasses used in commerce are made by fusing silica (sand) with two bases, one of which is usually soda or potash, and the other lime, lead oxide or other oxide of a divalent metal.

Commercial Importance of the Glass Industry

Before the 1914–18 war Germany was the most important producer of glass but in between the two wars she fell to second or third place, though her manufacturing capacity was only half utilised. In 1936 total world production is estimated to have been about 7½ million tons. The percentual distribution was: U.S.A. 40, U.S.S.R. 13, Germany 10, Britain 7.5, France 7, Japan 6.5, Belgium 3.5, Czechoslovakia 3, Italy 2, thirty-six other countries together 7.5. The breakdown of the German production, to take a specific case, of 727,000 tons for this year was: white blown and pressed hollow-ware 38 per cent., coloured bottles and containers 23 per cent., window glass 20 per cent., special flat glass 14 per cent., polished and rolled plate 5 per cent. Optical glass was negligible in weight but important in value. This production represented, on an average, only 51.5 per cent. of the German manufacturing capacity at that time. Since the war the manufacturing capacity of the Western Zones of Germany has increased compared with 1936 and is now practically 1,000,000 tons. In addition there is over 400,000 tons production capacity in the Russian Zone, and 100,000 tons in the territories under Polish administration. At the close of 1949 there were over 40,000 persons employed in the Western Zones and the average value (factory price) of the goods produced per head per month was 1000 DM in round figures. The production capacity of 998,000 tons was utilised to the extent of 76.5 per cent.

The number of persons employed in the glass industry in the U.S.A. at the beginning of 1950 was about 107,000 and the weekly pay-roll exceeded $27,000,000. Sales of table, kitchen and household glassware in 1949–50 were around 40,000,000 dozens. Glass to the value of $58,000,000 was exported from the U.S.A. in 1948, 69 per cent. going to North, South and Middle America, 7.3 per cent. to Europe, 16 per cent. to Asia, 7.3 per cent. to Africa and less than 1 per cent. to Australia and the South Pacific area.

British exports of domestic and fancy glassware in 1949 amounted to 172,000 cwt. with a value of £1,328,000, of which over 80 per cent. went to the Commonwealth countries. The value of exports has hardly changed since 1907 in which year they amounted to £1,400,000. In the same year British production was about £4,500,000 in value and imports about £3,000,000. At present (1952) production is running at about 1,000,000 tons per annum and some 70,000 persons are employed, compared with about 46,000 in 1936.

Those glasses which correspond in composition to definite chemical compounds are known technically as **normal glasses,** but it was for a long time thought that no truly normal glasses could exist, but that they would rapidly crystallise (*i.e.*, devitrify), and lose their characteristic properties. Later investigations, including those by Hovestadt, Zulkowski, and Fischer, have shown that many truly normal glasses can be prepared, if only the molecular weight is sufficiently high, and that these normal glasses have numerous advantages over those of merely approximately normal composition. Numerous normal glasses of the following compositions have been prepared, and have proved quite permanent and satisfactory:—

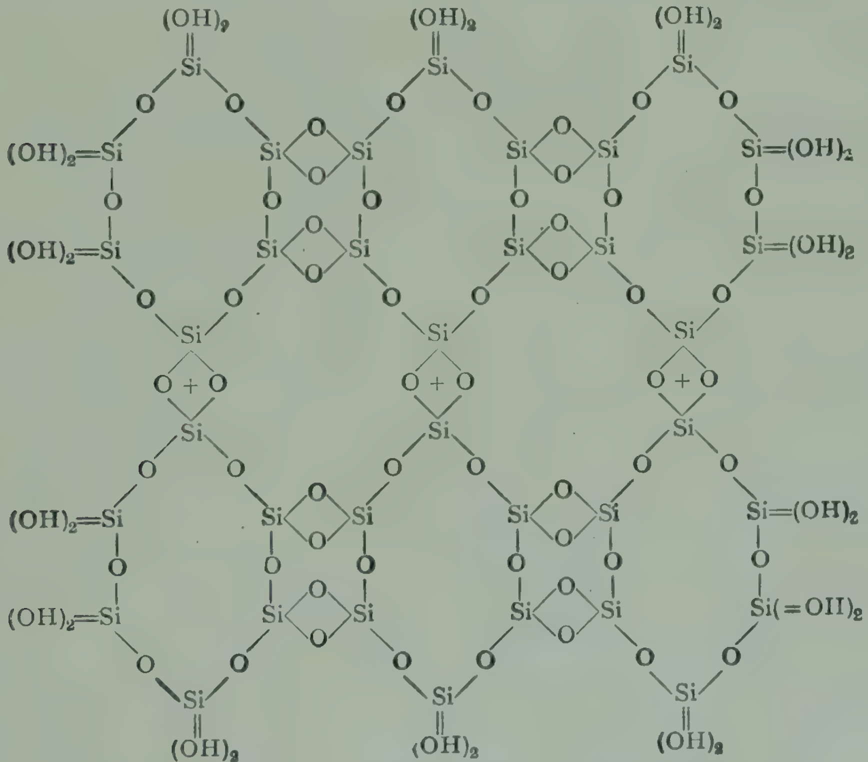
$5Na_2O.7CaO.36SiO_2$
$5K_2O.7CaO.36SiO_2$
$5K_2O.7PbO.36SiO_2$
$6K_2O.2PbO.2ZnO.BaO.36SiO_2$
$3Na_2O.3K_2O.3PbO.3CaO.36SiO_2$
$3Na_2O.3K_2O.6PbO.36SiO_2$

It is important to observe that Benrath, so long ago as 1875, showed that most useful glasses (other than optical ones) are included between the limits—

$$Na_2O.CaO.6SiO_2 \text{ and } 5Na_2O.7CaO.36SiO_2.$$

It is a matter of general experience that the simpler the composition and the smaller the number of atoms in the molecule, the more readily will the substance crystallise. This is equally true of the silicates, and is a further proof that the number of atoms in each molecule of glass must be much larger than is commonly supposed by those who represent the composition of glasses by the smallest possible number of atoms.[1]

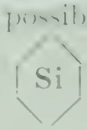
One of the earlier fruitful theories proposed in relation to the chemical constitution of glasses is that of W. and D. Asch, who suggested that glasses are complex silicic acids or the corresponding salts with 32, 36 or more silicon atoms in the molecule. For the primary acid with 36 silicon atoms in the molecule they suggested the formula—

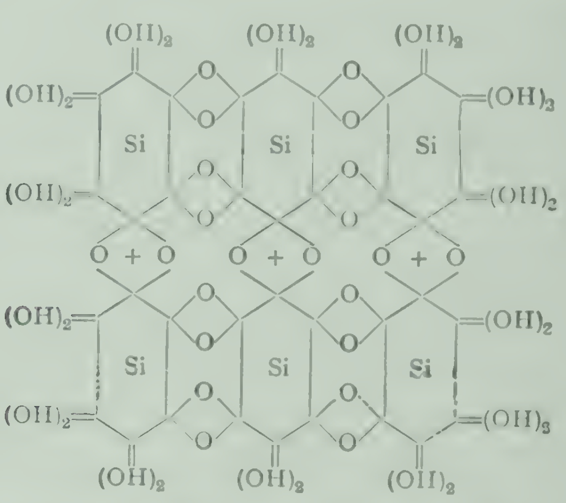


$14H_2O.36SiO_2$.

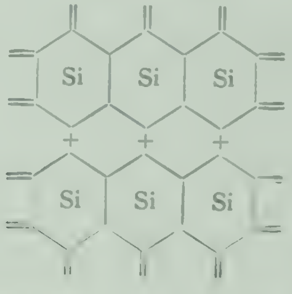
---

[1] As substances of low molecular weight crystallise readily whilst those of high molecular weight are difficult to obtain in a crystalline form, it is obvious that the properties desired in glasses will be obtained much more completely in a compound of very high molecular weight than in one of simple constitution. This is illustrated by the defect known as "devitrification," in which a simplification of structure occurs and crystals are produced.

In this formula the positions marked with a + are either direct bonds between the silicon rings or are those to which dibasic and sesquioxide forming elements may be attached. In this formula the maximum number of OH groups is shown, but a series of acids with fewer OH groups is also theoretically possible, and the H atoms in the OH groups can be replaced either in part or completely by sodium, potassium, calcium, magnesium, and various other metals. As these replacements occur exclusively outside the hexite rings formed by the silicon atoms, the formula may be simplified and its possibilities studied more readily by representing each Si_6O_6 group by the symbol , which reduces the formula to—

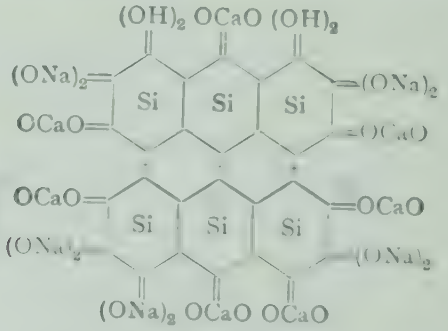


This may be still further simplified by omitting the hydroxyl groups but leaving the "bonds," and representing the complex group $Si_{36}O_{58}$ (which includes all the hexite rings and the connecting oxygen atoms) by



which, if fully hydrated, corresponds to the formula $14H_2O.36SiO_2$.

Using this diagram, the formula of a typical soda-lime glass is represented by



which corresponds to $2H_2O.5Na_2O.7CaO.36SiO_2$.

It is clear that many isomers of this substance are theoretically possible, and the precise arrangement of the various calcium, sodium, and hydrogen atoms must determine the properties of the glass, these properties being deducible from such formulæ, and confirmed by those actually found in the glass itself. For instance, it is clear that in the above formula some of the calcium atoms must behave differently from the others, and the same remark applies to the sodium atoms.

These formulæ also show why a good glass cannot consist of sodium and potassium as the sole metals, and that a monovalent and a divalent metal are both necessary otherwise Bennath's relationship would be upset.

Some of the silica rings can also be replaced by analogous ones of boracic, phosphoric, stannic, and other acids and their anhydrides, and various silica groups can be replaced by the anhydrides of stannic, titanic, zirconic and analogous acids. In this way a number of glasses of special properties may be produced, many of them being particularly valuable for optical purposes.

A considerable amount of further research is necessary before the precise positions of some of the various metallic atoms can be settled. This research must necessarily follow in directions analogous to those used with such conspicuous success in the study of the constitution of the crystalline silicates and simple glasses.

The positions marked with a + in the foregoing formulæ are highly important inasmuch as acid groups and metallic oxides (either in the **ous** or **ic** form) can enter the molecule there with remarkable effects on the properties of the glass, particularly as regards its colour and the action of light upon it. These positions are, in fact, the ones to which coloured glasses owe their special properties. Alumina is also assumed to enter here, one Al_2O_3 to each complex containing $36SiO_2$'s.

The views of the Asch brothers give evidence of remarkable ingenuity for the time at which they were enunciated. The new methods of structure examination initiated by v. Laue's discovery of the diffraction of X-rays by crystal lattices failed to reveal a three-dimensional periodicity in the glass lattice, which is now considered to have the form of a more or less random network of silica tetrahedra $(SiO_4)^{4-}$, in suitably sized meshes of which foreign cations, *e.g.*, Na^+, Ca^{2+}, etc., can be accommodated. The latter can be removed by appropriate means without destroying the network as a whole. They may be regarded as forming coordination links with the appropriate number of contiguous oxygen atoms (see Fig. 1).

According to present theory the elements can be divided into a number of groups, based on their electronegativity, in respect of glass formation. To the first main group belong the network formers, *i.e.*, those atoms which, alternating with oxygen atoms, form the irregular, three-dimensional network of the glass. In addition to silicon, which forms the basis of practically all commercial glasses, the following are considered to be actual or potential network formers in oxygen glasses, B^{3+}, Ge^{4+}, P^{3+} and P^{5+}, As^{3+} and As^{5+}, Sb^{3+}, Cb^{5+}, Ta^{5+}, and, to a limited extent, Be^{2+}, Al^{3+}, Zn^{2+}, Mg^{2+}, Fe^{3+}, Ti^{4+}.

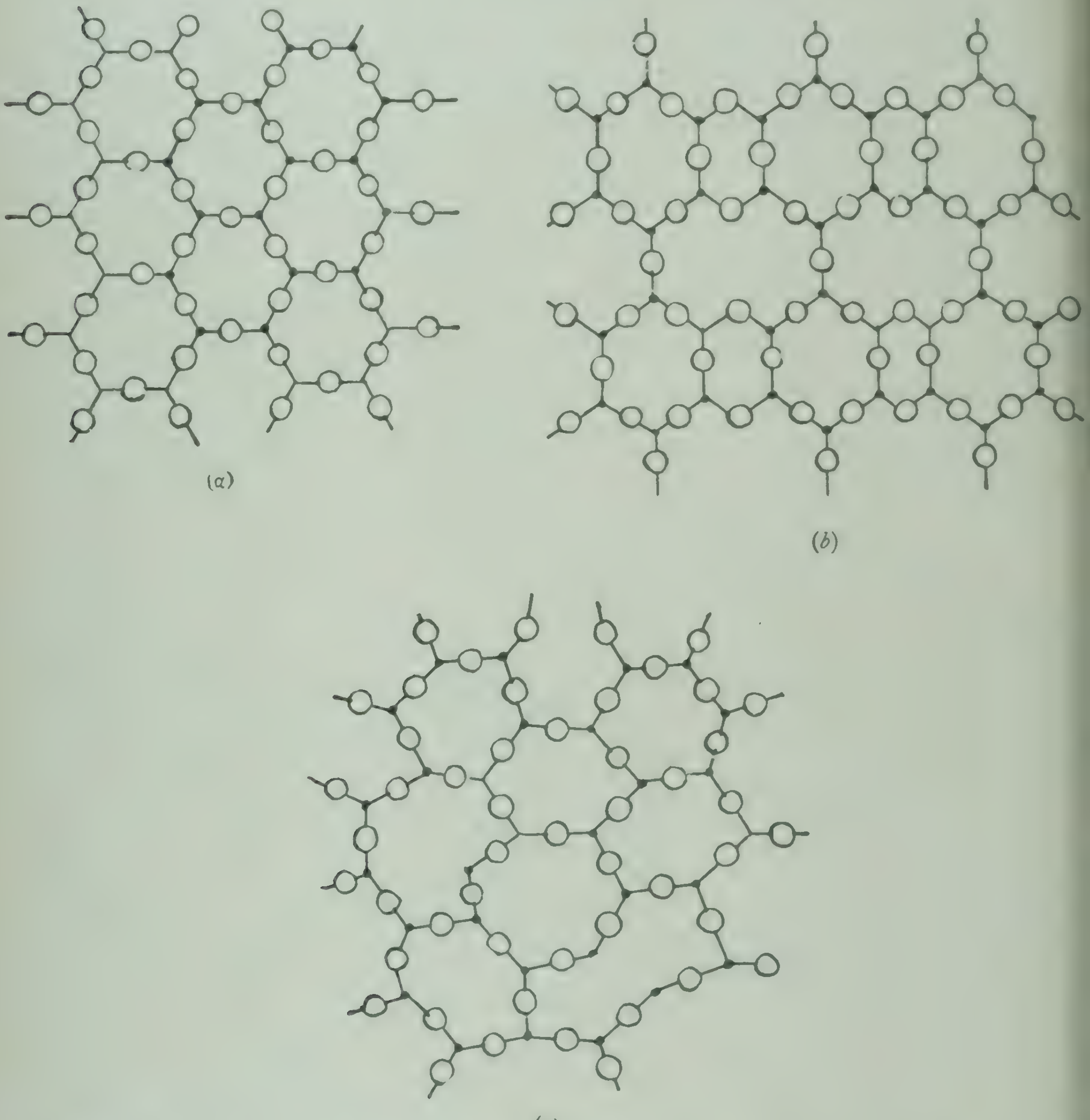
TABLE I.

DIMINISHING ELECTRONEGATIVITY OF ATOMS.

2.1 V	(2)	P	B	As	Si	Ge	Sb	Sn	Ti	Zr	Al	Be	Mg	Li	Ca	Si	Ba	Na	K	Rb	Cs	0.7
..		Network formers......................												Network modifiers........................								

The network-forming cations should have a small atomic radius compared with that of oxygen and a high electronegativity. They form bonds with oxygen which are ionic to the extent of not more than 50 per cent. or thereabouts. According to Smekal network formers have at least two coordination valencies.

The second main group contains the elements of the alkali and alkaline earth metals, which are of low electronegativity, have a comparatively large atomic radius and a high coordination number: the bond to oxygen is mainly ionic in character, viz. in the case of caesium to the extent of 85 per cent. The small and highly charged atoms Li^+, Be^{2+} and Mg^{2+} yield glasses with higher densities than would be expected: this is explained by the assumption that they actually cause a local contraction of the network at the interstices which they occupy.


(a)

(b)

(c)

FIG. 1.—Two dimensional network (Schematic) of SiO_2 tetrahedra in (a) crystalline silicate material, (b) the Asch brother's hypothetical complex silicic acid, and (c) a silicate glass. (a) Consists of coplanar six membered rings only, (b) of coplanar 4, 6, and 8 membered rings, (c) of non-planar rings of various sizes, including irregular shapes. (After Asch bros., Bragg, Zacchariasen, etc.)

With coloured ions the colour produced depends on the state of coordination of the ion, in the case of crystalline materials, and it is assumed that the different colours produced by the same colouring oxide in a given type of glass can be accounted for on the same basis. Thus, in the case of copper, four of the six atoms of oxygen in coordination positions appear to be more firmly attached than the other two and the colour depends on the degree of polarisation of the two less firmly bound oxygens.

If an oxidic glass is represented by the formula A_mB_nO, in which B represents the network formers and A the network modifiers, the value of n is usually about 0.4 unless boric oxide is present. In the latter case it may rise to 0.5 or a little more. The value of m is usually less than 0.3.

Similar considerations to those applied to the oxidic glasses lead to the conclusion that glasses may exist with other anions as the basis of the network, *viz.* F^-, which forms a glass with Be^{2+} as the glass-forming cation. Some of these glasses have special properties.

Glasses consisting of S^{2-} paired with cations larger and weaker than Si^{4+}, *e.g.*, As^{3+}, Ti^{4+}, Te^{2+} are good transmitters of infra-red. As_2S_3 glasses have proved particularly useful beyond 5 microns. They also have a high refractive index. S^{2-} may be replaced by Se^{2-} or Te^{2-}.

The effect of alumina on glass has been shown by Schott to increase the facility with which the glass can be worked in the blowpipe. Seger also studied the effect of alumina very thoroughly and found that it increases the fusibility, makes the glass easier to work, and greatly reduces the tendency to devitrify or crystallise. Many manufacturers have also found that the presence of a small proportion of alumina greatly improves the working power of the glass. It has hitherto been difficult to explain satisfactorily how so small a proportion of alumina (seldom more than 3 or 4 per cent.) could make so much difference. Various theories of catalytic action, etc., have been proposed, but the position of the two aluminium atoms in the foregoing formulæ explain the effect of the alumina on the glass far more simply and satisfactorily than any previously published theories: it binds the silicon rings together in a firmer manner than when no alumina or corresponding sesquioxide is present. Earlier writers on glass manufacture protested strongly against the use of alumina as making glass more difficult to fuse and increasing its tendency to devitrification. Later writers have expressed a different opinion, and Schott's experiments have shown that some alumina in a glass greatly improves its working properties, giving it special facilities for being worked in a blowpipe. The maximum proportion of alumina permissible is less than 10 per cent. of the weight of the sand used.

From the modern viewpoint aluminium may be regarded as capable of acting as a network former or modifier (or in part one, in part the other) according to conditions, in harmony with its chemical behaviour as an amphoteric oxide. In other words, it is capable of existing in 6-fold or 4-fold coordination in respect to oxygen atoms in the network. The peculiar behaviour of boron is also explained by reference to variation in its state of coordination.

The form in which the alumina is added to the glass-mix is important; clays are unsuitable, the best form being felspar or sands containing felspathic matter. Pure alumina may also be used, if desired, but is more costly.

The well-known fact that glass is attacked by pure water more strongly than by acids, and more by weak acids than by strong ones, may be explained by the use of the foregoing formulæ. It is probable that water alone causes primary alkali to be separated from the molecule, and this free alkali then reacts on the molecule and removes some of the silica, forming one or more five-atom rings or pentites, this reaction having been frequently observed by W. and D. Asch in other complex silicates. With strong acids, on the contrary, the alkali is immediately neutralised, and the secondary action is prevented.

The cause of the **devitrification** or crystallisation of glasses has long been a subject of investigation and theorising, but without much satisfaction. Gröger examined the devitrified glasses produced at a large Austrian works very thoroughly and found that the chemical composition of the amorphous and crystalline portions were identical, within the limits of accuracy of his analytical methods.

The chemical composition of the crystals separating from glass of any particular composition can be deduced from the phase-equilibrium diagram for the various oxides making up the glass. When the temperature of molten glass is allowed to fall below the liquidus curve of the equilibrium diagram it does not necessarily crystallise. It is the reluctance of glass to crystallise out which constitutes its most striking characteristic and makes its "working" possible. Should conditions be favourable to crystal formation, the crystals which do appear will be governed by the requirements of the phase diagram (see Fig. 2).

The size of crystal produced will depend on the time and temperature as well as the composition of the glass, and for any particular glass composition there is a more or less narrow temperature change over which the velocity of crystallisation passes through a maximum value. At temperatures appreciably above, no crystallisation can take place because the temperature is too high; at temperatures appreciably below, the viscosity is too high for the atoms or atomic groupings to rearrange themselves in the necessary ordered sequence in the time available. These relationships are indicated by the curve in the diagram (see Fig. 3).

The **temperature** at which devitrification takes place with maximum velocity is very close to that at which glass is worked, since the viscosity temperature curve is fairly steep in this region. The difference between the two may be taken as an indication of the safe working range of the glass: alternatively the slope or gradient of the curve at the upper devitrification temperature may be taken as an index of workability.

The following table gives the characteristics of crystals in **glass "stones"** arising from devitrification and some other common causes. (After Scholes.)

Name.	Composition.	Crystal System.	Crystal Habit.	Source.
Mullite - - -	$3Al_2O_3.2SiO_2$	Orthorhombic	Needles	Pot or tank walls
Corundum - -	Al_2O_3	Hexagonal	Basal plates	Pot or tank walls
Quartz - - -	SiO_2	Trigonal-Trapezoidal	Grains of indefinite shape	Batch sand
Cristobalite - -	SiO_2	Tetragonal (Pseudoregular)	Dendrites, twinned grains or lamellæ	Mainly devitrification, or spalls from SiO_2 brick
Tridymite - -	SiO_2	Orthorhombic (Pseudohexagonal)	Hex. basal plates or arrow-shaped twins	Devitrification spalls or scum
Devitrite - -	$Na_2O.3CaO.6SiO_2$	Orthorhombic	Prisms, needles, sheaves or spherulites	Devitrification in cooler regions
Wollastonite - -	$CaO.SiO_2$	Monoclinic	Needles, rods, prisms	Devitrification
Pseudo-Wollastonite	$CaO.SiO_2$	Monoclinic (Pseudohexagonal)	Six-sided grains, twinned lamellæ	Devitrification
Nephelite - -	$Na_2O.Al_2O_3.2SiO_2$	Hexagonal	Grains	Devitrification or stones from aluminous refractories
Carnegeite - -	$Na_2O.Al_2O_3.2SiO_2$	Triclinic	Lamellar twinning	Devitrification or stones from aluminous refractories
Diopside - - -	$CaO.MgO.2SiO_2$	Monoclinic	Grains	Devitrification

In special cases, mainly due to local abnormalities in composition in the glass, anorthite, albite, willemite, barium silicate and others are possible.

The wide variety of possible products of devitrification together with the difficulties of obtaining accurate analyses are doubtless responsible for many contradictory findings of earlier workers.

Blisters and **seeds** in glass are bubbles of gas which may result from careless gathering or inadequate check refining respectively. Seeds are avoided in tank practice by maintaining a sufficiently high temperature in the melting end and allowing the glass to remain in the melting chamber long enough to allow the bubbles (essential to proper mixing in the early stages) to rise to the surface and escape.

Recent investigations have shown that when glass is warmed to 300° C. and subjected to a current of electricity, it becomes electrolytically dissociated at the respective electrodes. Glass is so poor a conductor that the amount of dissociation is very small, though it is quite perceptible when mercury electrodes are used, sodium amalgam being formed at the cathode. The composition of the anode-ions has not been ascertained; but it has been proved that no gas is evolved at the anode, so that the most probable result of the electrodes is merely to remove some of the sodium leaving a more refractory glass. On heating the electrolysed glass *in vacuo* to its softening point it becomes turbid and an evolution of oxygen occurs equivalent to about one molecule of gas to three molecules of sodium at the cathode.

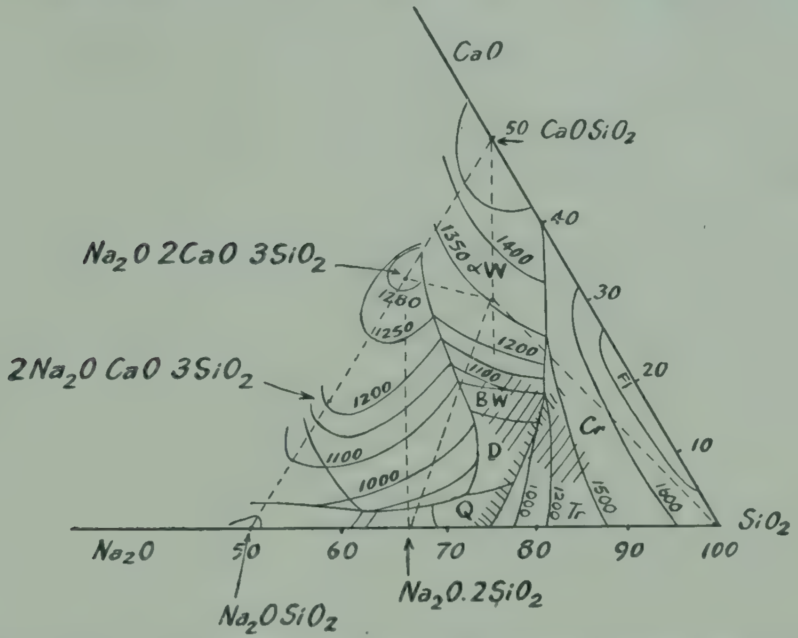


FIG. 2.—Technically important area of $Na_2O/CaO/SiO_2$ diagram with areas of maximum durability ///// and minimum crystallisation tendency \\\\\ shaded in. (Jebsen-Marwedel, after Morey and Bowen).

Fl = 2 immiscible liquids.
Tr = Tridymite.
W = Wollastonite.
Cr = Cristobalite.
Q = Quartz.
D = Devitrite.

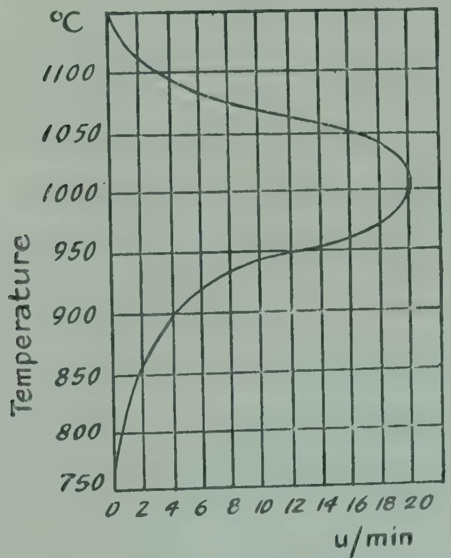


FIG. 3.—Crystal growth rate as function of temperature. (Jebsen-Marwedel after Zschimmer and Dietzel.)

When a glass is heated, it passes through all degrees of viscosity until it becomes quite mobile, there being no sharply defined temperature at which it changes definitely from solid to liquid. Even at temperatures at which they appear to be solid, glasses are deformed gradually under severe stresses, though under a sudden stress they act as brittle solids. Parker and Dalliday have found that the rate of deformation under constant stress is an exponential function of the temperature, the equation representing it containing an expression which varies with the composition of the glass. This absence of a well-defined melting point merely indicates that the constituents of glass have been under-cooled; it does not necessarily show that glass contains more than one essential constituent as the supporters of the "mixture" theory suggest. Phenol and many fused organic compounds of known constitution behave like glass if cooled too rapidly for crystallisation to occur, or in the presence of small proportions of impurity, yet it is never suggested that such compounds are "mixtures" or "solid solutions."

The temperature viscosity curve for a soda-lime glass suitable for machine blowing is shown in Fig. 4 (after Lillie). The dependence of viscosity on temperature may, according to Le Chatelier, be represented by a formula of the following type:

$$\log \log \eta = M\left(\frac{\theta - 1000}{1000}\right) + N, \text{ where}$$

M = coefficient of viscosity increase,
N = viscosity at 1000° C.,
η = ,, ,, temperature θ.

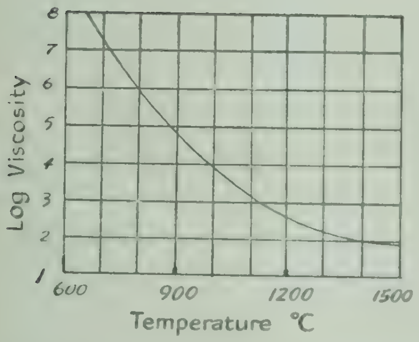


FIG. 4.—Temperature / Viscosity Curve for Soda Lime Glass. (after Lillie.)

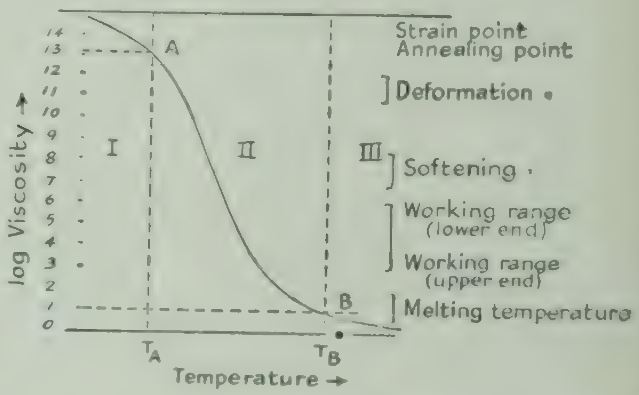


FIG. 5.—Physical State and Viscosity Values.
I = Brittle. II = Viscous. III = Liquid.
A = Transformation pt. B = Aggregation pt.
(after Horowitz.)

The general shape of the curve and the physical state of glasses at various viscosity values are depicted in Fig. 5 (after Horowitz).

The upper annealing temperature in Fig. 5 is the temperature at which all strain disappears within 2 minutes; the lower annealing temperature is one below which all strain will not disappear in 4 hours. It is, in general, not more than 150° C. below the upper annealing temperature. For most glasses the annealing range lies between 425° and 600° C. Lillie defines the lower annealing temperature as that at which the viscosity has the value 4×10^{14} poises. The softening point of a glass, *i.e.*, the temperature at which a filament of specified diameter and length heated at a given rate elongates under its own weight at a rate of 1 mm. per minute, runs about 100° higher than its annealing point.

The glass division of the American Ceramic Society in 1947 defined the annealing point as the temperature at which internal stress is substantially relieved in 15 minutes. The corresponding viscosity is 10^{13} poises.

Melting temperatures of some glass types are shown below:—

Phosphate glass	1,000° C.
Heavy lead silicate (flint) glass	1,100° C.
Borate glass	1,130° C.
Heavy barium boro-silicate glass	1,320° C.
Ordinary flint glass	1,370° C.
„ crown glass	1,410° C.
„ white hollow-ware glass	1,350° C.
Quartz glass	1,700°–1,800° C.
Water glass	1,500° C.
Enamel frit	1,090°–1,400° C.

The heat required to melt glass varies with the type of furnace, the fuel used, and the nature of the glass. Average values for sheet glass in tank furnaces range from 4,500–7,700 Kcal./kg. (8,100–13,860 B.Th.U./lb.), though values as low as half the former figure are claimed for particularly efficient tanks. The values given include producer losses. Oil-fired furnaces are claimed to give lower heat consumption, *i.e.*, higher thermal efficiency, than producer gas furnaces. For electric melting still better results are claimed. As fuel costs amount to between 20 and 30 per cent. of the total manufacturing costs the importance of economic firing needs no stressing.

The Table on p. 264 gives the average analyses of a number of typical glasses.

At first sight these analyses do not appear to indicate very definite compounds, but a careful calculation of the formulæ will show that (allowing for included impurities) the majority of them correspond fairly closely with one of the following formulæ:—

$$aR_2O.bRO.36n(xSiO_2+yB_2O_3)$$
$$cR_2O.dRO.30n(xSiO_2+yB_2O_3)$$

(where n indicates unity or an integer).

It is interesting to compare these analyses with the formulæ given on pp. 255–256. It is also well to bear in mind that the presence of a small proportion of impurity will often prevent a substance from crystallising; this well-known fact is largely used in glass manufacture, and the strict adherence to the proportions of raw materials likely to produce glass of completely "normal" composition is, therefore, avoided by many glass-makers.

From the formulæ shown above and on previous pages it follows that the proportions of the various ingredients used in the manufacture of glasses must be confined within somewhat definite limits, and experience has shown this to be the case. Thus glasses containing more than 80 per cent. of silica are of no commercial value, as they are very difficult to fuse and devitrify readily; the successful production of articles from a fused mass of almost pure silica suggests, however, that a more extended research on these highly siliceous glasses may show that the devitrification is largely due to the use of an excess of metallic oxide rather than the impossibility of producing glasses with more than the percentage of silica just mentioned. That certain proportions of metallic oxide and silica will produce an unstable glass which readily devitrifies into a stable crystalline compound and a stable amorphous glass is readily prognosticated from the formulæ mentioned, but this can occur with any proportion of silica and is not confined to those glasses in which the proportion of silica is unusually high. Experience has shown that the composition of the mixtures used for glass-making must be accurate within narrow limits, though the results of analyses of the finished glass do not correspond to the proportions of the raw materials used, it being almost impossible to make due allowance for the removal of scum, the action of the glass on the pots or furnace and the loss which occurs through volatilisation. This last will usually amount to about 6 per cent. of the alkali used, apart from the more readily recognised volatile constituents. It can be diminished by charging the batch moist.

	SiO_2.	B_2O_3.	Na_2O.	K_2O.	CaO.	MgO.	BaO.	PbO.	ZnO.	MnO.	Al_2O_3.	Fe_2O_3.	As_2O_3.	P_2O_5.
Best table glass	70.70	...	10.02	8.62	10.02	...	...	...	...	...	0.43	0.21	...	...
St Gobin glass	77.15	...	15.38	...	7.47	...	...	...	...	...	...	...	...	...
Venetian glass	73.40	...	18.58	...	5.06	...	...	...	...	...	2.50	0.40	...	...
English sheet glass	72.42	...	13.13	...	11.97	...	...	...	...	...	2.13	0.35	...	...
Best plate glass	71.80	...	11.10	...	15.70	...	...	...	...	...	1.20	0.14	...	...
Pressed glass	70.68	...	19.08	...	5.45	...	4.17	...	...	...	0.33	0.24	...	...
Bohemian glass	71.70	...	2.51	12.74	10.32	...	...	...	...	...	0.22	0.51	...	...
Ordinary flint glass	53.17	...	...	...	13.88	...	...	32.95	...	...	...	...	...	...
Champagne bottle glass (A)	58.40	...	9.90	1.80	18.60	...	...	...	...	...	2.10	8.90	...	...
Champagne bottle glass (B)	56.68	...	9.40	1.13	19.87	6.42	...	...	...	...	4.07	1.93	...	...
Common bottle glass	63.51	...	9.50	...	14.32	3.87	...	...	...	2.90	2.54	2.30	...	...
Jena laboratory glass	65.30	15.00	...	...	...	...	12.23	...	...	...	3.80	0.41	3.20	...
Jena thermometer glass	67.50	2.00	14.00	...	...	7.00	...	...	7.00	...	2.50	0.50	...	...
Jena boro-flint (S 57)	...	58.00	...	...	...	...	...	32.00	...	...	10.00	...	...	...
Jena phosphate crown (S 40)	...	3.00	...	...	...	28.00	...	...	...	...	8.00	...	1.50	59.50
Good Thuringian glass	67.74	...	16.01	3.38	7.38	0.27	...	...	...	...	3.38	...	...	...
Bad Thuringian glass	66.90	...	16.50	6.60	3.80	0.10	...	...	...	0.40	2.40	0.60	...	...

---

[1] The suggested limits for champagne bottles (see p. 275) correspond to 0·6R_2O, 1·2-1·8RO, 1·6R_2O_3, 36SiO_2. Glass for common bottles is not so rich in lime, and the usual limits for it correspond to 0·6R_2O, 0·6-1·8RO, 1·3R_2O_3, 36SiO_2.

It is now generally admitted that the following molecular ratios express the limits between which most commercially useful glasses fall:—

	Alkali (R_2O).	Lime, Lead, etc. (RO).	Silica (SiO_2).
White glass for table ware	5·9	6	30·60
Bohemian crystal glass	Under 12	6	30·90
Plate glass	4·6	6	24·36
Flint glass	2·6	6	20·36
Bottle glass	(Limits very variable.[1])		

The **properties** of glasses are greatly influenced by the treatment they receive during various stages of manufacture and in the subsequent storage. If cooled too rapidly, glass becomes brittle and liable to fall to powder of its own accord on account of the internal strains to which it is subject.

This is well shown by the behaviour of **Rupert's drops** which consist of drops of glass which are cooled very rapidly by allowing the molten glass to drop slowly into water. The interior of the mass is in a state of intense strain owing to its rigidity having been prevented by the cooling contraction of the more rapidly cooled outer layer. Hence the breaking-off of even a minute portion of the drop will cause the remainder of the material to fall to powder with almost explosive violence.

Hot glass is so **viscous** that it may be rolled like dough; it may be blown into hollow vessels by the pressure of the human breath or by mechanically compressed air; it may be moulded into various shapes by placing it in an iron mould and blowing into the glassy mass so that it expands and occupies the whole of the mould (this operation of shaping by means of moulds is technically known as pressing; it may be effected by means of a plunger where solid articles are desired). Hot glass is also so ductile that it can be drawn out into extremely fine threads of a beautiful silky lustre and capable of being woven into a fabric. These extremely fine filaments are known as **spun glass.** If the mass of glass is hollow before being drawn, tubes or pipes will be produced; these are used for a variety of purposes, particularly in chemical laboratories.

Glass tubing and **rod** is now almost entirely produced by automatic machines, hand making being resorted to only when small quantities of "specials" are required, *e.g.*, unusual diameters or wall thicknesses, or unusual compositions or colour combinations. In the automatic machines the molten glass flows over a rotating refractory sleeve through which air is blown into the interior of the tube. The tube is pulled by being gripped, at a point where the glass is rigid, between asbestos pads on two endless chains running on sprockets; it is automatically cut into lengths. Linear speeds up to several hundred feet per minute, depending on diameter and wall thickness, may be attained. The change-over to rod may be effected by shutting off the air-current. In the hand method a ball of glass is gathered from a furnace on a blow-iron and after suitable shaping is "stuck-up" on an iron post carried by an assistant, who gradually walks away while the operator blows air in at intervals. A second assistant gauges the diameter of the glass while it is being drawn and regulates the drawing out to some extent by fanning the tube where it needs more rapid cooling. The men are paid only for tubing of the correct size and become extremely skilful. Glass rod is drawn in a similar fashion except that there is no blowing, the gathering being done on a solid iron.

Fibre glass is a development of spun glass, which received its name from the process of collecting it over a spinning wheel or drum. **Continuous filament fibre** is drawn from molten glass in electric furnaces through fine multiple nozzles at a linear rate of over a mile per minute. The individual filaments have a diameter of about .0002 in. and are automatically twisted into a strand of about .002 in. diam. This can then be twisted into still coarser yarn or woven into braid, tape, etc. **Staple fibre** is produced by projecting a powerful blast of air or steam against the molten glass emerging from the furnace through fine orifices. Ordinary glass wool in bulk is formed in this way. It finds application in heat, electrical, and sound insulation, in filtration of air and solutions, in making fireproof fabrics, in reinforcing laminates, in battery retainer mats, in a glass rayon bandage for fractures, etc.

Homogeneity is an essential characteristic of all good glass. It is exceedingly difficult to secure, particularly in furnaces arranged to give a continuous supply of glass, though much may be done by carefully adjusting the sizes of the melting pots or tanks and by heating the glass to a sufficiently high temperature.

A prominent characteristic of glass is its **transparency,** though this differs greatly with different specimens, some being purposely rendered opaque by the addition of infusible matter, whilst others are opaque to certain rays of light. Most ordinary glass is opaque to ultra-violet and infra-red rays; especially if it is rich in lead. Other glasses are now made which are transparent to particular parts of the spectrum, and to X and other e.m. radiations. It is well known that the transparency or opacity of such glasses depends upon their composition. The optical properties of glass are largely due to its transparency, but are more conveniently considered separately (p. 263).

The effect of prolonged heating on glass is to tend to make certain compounds crystallise out. This fact is used technically in the production of a semi-opaque glass known as **ambitty,** which consists of ordinary glass permeated with microcrystalline matter in such a manner as to deprive the mass of its normal transparency, and to render it semi-opaque.

The **density** or specific gravity of glass varies with the molecular weight of the constituents, and ranges from 2.25 for the lightest borate glasses to 6.5 for the specially dense lead-barium glasses. Ordinary glass has a specific gravity of 2.45 to 3.00, and does not vary appreciably with the composition, so long as lead and barium are not among its constituents.

On heating, the specific gravity is reduced, but the **expansion** of glass is very irregular and varies greatly with different types of glasses.

For soda-lime glasses the mean coefficient of expansion lies between 0.000023 and 0.000027 per 1° C. The expansion of glass becomes important in the manufacture of thermometers and some other scientific apparatus, and also in the manufacture of lenses and other articles in which two different glasses are fused together. It is even more important in the manufacture of flashed window glass, enamelled glass, and in those cases (*e.g.*, electric lamps) where metal is fastened to glass. Various methods of reducing the irregularity of expansion are now used in the manufacture of scientific apparatus, but a description of these is beyond the scope of this work.

Glass of low expansion is very viscous, and if boric oxide is used to overcome this, it tends to make the glass soluble in water.

The **elasticity** and the **compression strength** of glass are high, but the **tensile** and **impact** strengths are relatively low by comparison. This combination of properties accounts for the characteristic brittleness of the material. Fine fibres yield extremely high strength figures owing to the absence of sub-microscopic cracks (Smekal cracks) which are starting-points for mechanical failure.

The **thermal endurance,** or resistance to sudden changes of temperature or to prolonged heating, possessed by glasses appears to depend partly on their composition and partly on the treatment they have received.

Readily fusible glasses are the most sensitive, and the nearer a glass approaches the composition of pure silica the more readily will it endure thermal treatment. In this respect, glasses resemble the more refractory clays and siliceous rocks, though the endurance of the latter is much greater than that of glass.

The mean specific heat of glass is 0.177 from 0°–100° C., and 0.190 from 0°–300° C.

Glass is a particularly bad conductor of heat, and therefore requires a considerable time for it to become heated uniformly. This is one cause of it cracking: it is so difficult to secure a uniform distribution of the heat unless the glass is exceedingly thin.

The **melting point** of glasses varies with their composition, but their conductivity is so low that it is difficult to obtain a sharp melting point, and this difficulty is increased by the presence of impurities and by the atomic changes glasses undergo on prolonged heating at temperatures near to their melting point.

For most commercial purposes, glasses must melt between 1,300° and 1,500° C., but they must remain pasty or viscous at temperatures far below this in order that they may be worked conveniently into the articles it is desired to produce. Where cheapness is the chief consideration, a readily fusible glass is preferred, but such glasses lack the permanency of those of a more refractory character, and tend to devitrify and to be unduly corroded by water and other fluids. The most infusible glass[1] is pure silica which can only be fused in the oxy-hydrogen blowpipe flame, or in an electric furnace at a temperature of 1,800°–2,000° C., though it becomes soft and viscous at 1,600° C. Glasses which contain both soda and potash are more readily fusible than those which contain only one of these oxides.

Melting point here means the temperature required to melt the batch at a commercially desirable rate.

The **hardness** of glass depends partly on its composition and partly on the rate at which it has been cooled. Generally speaking, the higher the proportion of silica, lime, and alumina the harder will be the glass, but glasses rich in lead and soda or potash are frequently soft. Curiously enough, the soda glasses are usually harder than the potash ones. All glasses which have been cooled rapidly are covered with a film of harder material than the interior, but this is accompanied by such severe strains in the glass as to make the latter almost useless.

These strains may be avoided, as suggested by Schott, who surrounds the glass with another of less expansibility, so that both the exterior and the interior glasses are hardened. Another method, much in use at present, consists in placing the glass between two metal plates, so as to secure a rapid and uniform loss of heat from every part of the surface and to prevent the edges cooling first. Copper sheets give the hardest glass, iron sheets being inferior for this purpose.

In 1874 M. de la Bastie published a method of hardening glass which has not, however, become popular. It consisted in immersing the hot glass in oil at a temperature of 300° C., and then allowing it to cool very slowly to the ordinary temperature. Such glass can be dropped without breaking and is capable of standing very sudden changes in temperature. Its weakness lies in its unreliability, for if the smallest particle of glass is removed from the surface, as by a minute scratch, the internal forces in the glass are set free and it falls to pieces with explosive violence (*cf.* Rupert's drops, p. 265). Such glass cannot be cut or ground. Any cutting or shaping must be done before the glass is toughened or disannealed. Lenses for spectacles or goggles, tumblers, and window screens for motor cars can be toughened by this means. Blasts of cold air may be used for quenching from temperatures within the annealing range. The fact that such toughened glasses disintegrate into comparatively small particles on failure may be an advantage, *e.g.*, in window screens on motor vehicles.

---

[1] Some authorities object to fused quartz being regarded as a glass, and it is therefore treated separately on p. 299.

The **brittleness** of glass is a characteristic property, which appears to be associated in some way with the considerable difference in the mechanical strength of SiO_2 under pressure and tension. It reveals itself in a sudden failure of the material when deformed fairly rapidly beyond the elastic limit, in contrast to metals, where the breakdown only follows an initial state of adjustment to the deforming force by flow. At temperatures above the transformation point the elasticity of glass gives way to a more or less rapid plastic deformation under the influence of the applied stress.

The **Chemical Properties of Glass.**—A most important feature of the technically valuable glasses is their inertness and resistance to chemical action. At the same time, no glass is completely resistant, the actual decomposition taking place depending on the reagent to which the glass is exposed, the composition of the glass, and whether it is in a state of powder or a polished surface is alone exposed.

In this connection, some very unexpected results may be obtained; thus, as previously mentioned, glass is more resistant to strong acids than to weak ones, and more resistant to weak acids than to water (p. 259). Glasses with a large proportion of soda or potash (some authorities say 15 per cent.) are unsuitable for chemical purposes on account of the ease with which they are attacked. Many excellent optical glasses suffer somewhat from the ease with which they are decomposed by moisture condensing on them. Boro-silicate crown glasses are the most resistant to chemical action, and are therefore of special value for laboratory ware. Superheated water has a powerful action on all glasses, decomposing most of them to such an extent that all the contained alkali is removed, and leaves a calcium or lead hydro-silicate. It is difficult to understand the behaviour of superheated water if the earlier theory that glass is a mixture of simple silicates is maintained. If, on the other hand, glasses are ring compounds similar to those for which formulæ are given on p. 239, the action of water is readily explained. The sodium and potassium groups are replaced by hydroxyl ones, but the calcium groups, being more firmly bound to the molecule, are not attacked.

Strong acids have little or no appreciable action on most glasses, though some optical and other glasses rich in alkali are readily attacked. The only exception to this is hydrofluoric acid, which unites with the silica to form a volatile silicon fluoride, and brings about a complete decomposition of any glass. Highly basic glasses are less attacked by dilute acids then glasses richer in silica; this is only true, however, if the basicity of the glass is due to oxides of the RO type, and not to those of the R_2O group.

Alkaline solutions attack some glasses more energetically than water or acids, as they displace some of the weaker bases, and break up the glass molecule into simpler silicates.

Atmospheric influences have an important effect on window and other glasses unless special care is taken to produce a sufficiently resistant material. The most potent factor is the action of condensed moisture on the glass, but the use of soaps containing alkali for cleaning the glass is also important in effecting its deterioration.

The precise influence of the atmosphere on a given glass is very difficult to determine. It is usually tested, as suggested by Mylius,[1] by exposing a carefully cleaned sample of the glass to the action of water for a definite period, and then treating it with an ethereal solution of iodo-eosin. The intensity of the red deposit produced by the alkali set free is dissolved in water, and the colour of the solution is compared with that produced by the use of known quantities of alkali. Another method consists in determining the loss of weight suffered by the glass when treated with water or with N/1 acid, and affords another indirect means of determining the resistance of the glass. Mylius and Förster found that 20 g. of glass powder, from which the finest particles had been removed, when boiled with 70 c.c. water for five hours lost the following weights:—

---

[1] *Zeits. f. anorg. Chemie*, 67, 200, 1910.

$6Na_2O.6CaO.36SiO_2$	7.4 mg.
$9Na_2O.3CaO.36SiO_2$	42.4 ,,
$10.5Na_2O.1.5CaO.36SiO_2$	507.6 ,,
$6Na_2O.6CaO.30SiO_2$ (Rhenish window glass)	8.4 ,,
$5Na_2O.0.5K_2O.8CaO.3.5MgO.34SiO_2$ (green window glass)	6.5 ,,
$0.5Na_2O.3.5K_2O.3CaO.34SiO_2$ (Bohemian chevalier glass)	10.1 ,,
$4Na_2O.K_2O.CaO.34SiO_2$ (defective Thuringian glass)	91.4 ,,
$6K_2O.6PbO.36SiO_2$ (lead glass from Ehrenfeld)	8.5 ,,
$7Na_2O.4CaO.3ZnO.36(SiO_2+B_2O_3)$ (Jena thermometer glass)	6.4 ,,

THE RAW MATERIALS USED FOR GLASS-MAKING

As will have been understood from the foregoing remarks on the composition and general properties of glasses, the raw materials are essentially of two kinds: (*a*) substances of an acidic nature such as silica and boric acid, and (*b*) substances of an alkaline or basic nature such as soda, potash, lime, magnesia, baryta, zinc oxide, lead oxide, etc. Some glasses also contain other materials, the behaviour of which it is less easy to define, such as alumina and oxide of iron, both of which attach themselves to the glass network, but in a different position to those occupied by the substances previously mentioned (see the formulæ on p. 256). Various decolorising and opacifying agents are also added when desired.

Glasses are essentially salts of complex silicic acids, the combination of the acid and base occurring only at a temperature of 1,300° C. or above. At this temperature, however, many other acids combined with such alkalis and bases as soda and lime are decomposed, so that it is possible, in the manufacture of glass, to use the cheaper salts of the alkalis and bases rather than the bases themselves. Thus chalk or limestone are both decomposed at a temperature of about 700° C. into free lime, and as chalk and limestone are much cheaper than quicklime they are used by the glass-maker as a source of the latter material. This fact must be borne in mind in considering the raw materials employed and suitable adjustments made to the batch weights.

Silica is used in the form of sand, the purest available sands being used for the better qualities of glass, and somewhat less pure sands for the cheaper bottle glasses.

The purest English sands are obtained from Lancashire, Bedfordshire, and King's Lynn; the cheaper sands may be used from the locality in which the works are situated. The French glass-makers use Fontainebleau sand, which contains 99.98 per cent. of silica; the best English sands are slightly inferior to this, but selected portions reach this very high standard. In Bohemia, crushed quartz is used. Suitable sands containing feldspathic material are found in some parts of Germany.

It is very important that the sand should be sufficiently pure, as even a small proportion of some ingredients will prevent good glass being made from it. Thus for sheet glass for windows not more than ½ per cent. ferric oxide is permissible, and for coarse bottle glass 2 per cent. or more will do no harm, but for the finest white crystal and plate glasses the iron in the sand ought not to exceed 0.1 per cent

Soda is usually employed in the form of **sodium sulphate,** a little carbon being mixed with it to facilitate the reduction of the sulphate, except in the case of lead or flint glass.

Sodium carbonate is equally satisfactory for the purpose but is more costly, though the wise glass maker keeps a sharp look-out on the relative prices of these two forms of soda. Sodium sulphate requires a higher temperature than the carbonate before it begins to react with the silica, and more of it is required (about seven parts of the sulphate are equivalent to five parts of the carbonate), so that it is only when the sulphate is less than half the price of the carbonate that its use is profitable. The sulphate and carbonate radicles play no part in the manufacture of the glass, as it is only the metallic radicle which is important. **Common salt (sodium chloride)** cannot be used on account of its great volatility which makes it commercially too expensive: otherwise it reacts with silica quite as effectively as the other sodium compounds just mentioned.

Sodium sulphate should never be used in highly coloured glasses as these require a larger proportion of colouring agent than when sodium carbonate is used.

Potash is used in the form of **potassium carbonate,** as this is the cheapest and most available form. In lead glasses (flint glasses) and in some coloured ones where an oxidant is required, some potash is introduced in the form of **nitre** (potassium nitrate), but this is too expensive for general use.

Substitutes for nitre have recently attained considerable importance. The most suitable are **barium peroxide** (see p. 271), **potassium chlorate** and **perchlorate.**

Lime, as already mentioned, is used in the form of carbonate (either **limestone** or **chalk**), but the **hydrate** is occasionally employed.

It is important to avoid the use of dolomitic limestone, as this contains magnesia which increases the viscosity of the glass, and prevents it being so clear as when a purely calcareous limestone is used. Nevertheless a small proportion of magnesia in glass is now considered to make it more suitable for use in automatic making machines owing to its effect on the viscosity *v.* temperature relationship.

Lime (and its compounds) is the most uncertain ingredient of all glasses, and it is responsible for a large proportion of losses in manufacture.

Magnesia is not a common constituent of glasses, except in minute quantities as an impurity. When purposely added it is introduced in the form of lightly **calcined magnesia.** Nowadays dolomite is also used in large scale production.

In French hollow-ware the proportion of magnesia is sufficiently large to be important. It is not added purposely, but is due to the use of dolomitic (magnesian) limestone instead of a pure calcareous stone. Magnesia makes the glass more difficult to melt but increases the range of temperature through which it can be worked. The great objection to its use in large proportions is that glasses containing it are difficult to heat sufficiently to make them properly fluid in the refining stage, so that they do not "clear" properly unless special precautions are taken. Magnesia also increases the tendency of glass to devitrify. In proportions of less than 10 per cent., the effects just mentioned are unimportant, and are counterbalanced by the strength and resistance to water possessed by glasses containing magnesia.

The magnesia molecules occupy the same positions in the glass network as those of lime, but if the lime is entirely replaced by magnesia a glass is obtained which has so rapid a rate of crystallisation that it devitrifies too much to be commercially valuable.

Zinc oxide may be used to replace lime and occupies the same positions in the glass molecule. It increases the refractive index of glasses, but not nearly so much as lead or baryta. Zinc oxide produces glasses with a small coefficient of expansion, great strength, and very low solubility in water and is, therefore, valuable as a constituent of laboratory glass and for thermometers. It cannot be used in large proportions, as zinc glasses devitrify with great rapidity.

In this connection it is interesting to notice that the addition of zinc oxide to pottery glazes is one of the easiest means of producing the beautiful crystalline effects which are so much admired. Zinc oxide tends to produce a yellow colour in glass, especially if the latter is overheated; this can be neutralised by a small proportion of nickel oxide.

The presence of zinc oxide in a glass lightens the labour of working by making the glass more ductile; it gives sharper outlines to moulded or pressed glass and a better finish. At the present time, however, it is chiefly confined to laboratory and optical glass and to that for thermometers.

Barium oxide or **baryta** is characterised by the high atomic weight of the metal it contains, and in consequence of this it gives density and lustre to glasses in which it occurs. It raises the melting point of mixtures in which it is present, so is not used for the commoner kinds of glass, but is greatly valued for special ones.

Baryta was first used in glass mixtures in 1829 by Doebereiner, but it is only recently that its valuable qualities have been recognised. It is chiefly used in hollow-ware, crystal-ware, special glasses, and for pressed glass. For the last named it confers just those qualities which are most desired, and is specially used to replace part of the lead. For plate glass, its use is accompanied by difficulties which have not, at present, been overcome. The chief drawback to the use of baryta is its tendency to devitrify in the absence of zinc oxide, and to settle to the bottom of the molten glass.

It is customary to employ precipitated **barium carbonate** as the means of introducing barium, as the sulphate induces an opaque frothiness which is not easy to remove. At the temperature of reaction, the carbonate and sulphate have both decomposed, and the active material is barium oxide. In many ways baryta behaves like lead oxide in the glass and may replace lead or lime but not alkali.

Barium peroxide (BaO_2) has proved to be a very satisfactory substitute for nitre. It has the advantage of evolving oxygen at a higher temperature than nitre.

Lead oxide is one of the chief constituents of flint glasses. Several oxides and carbonates of lead exist, but the one generally used by glass-makers is **red lead**, Pb_3O_4.

It is often contaminated with brick dust and other adulterants and should be tested before use. Lead compounds are easily reduced, and in the manufacture of flint glass it is necessary to avoid reducing conditions in the furnace. For this reason the addition of oxidants (such as nitre, p. 248) is usual. Lead glasses are improved by chilling in water and re-melting (**dragading**), as the additional heating converts them into more stable ones, possibly isomeric with those produced in the first heating.

Boracic or **Boric Acid.**—The chief characteristics of boracic acid are similar to those of silica, but the glass produced is much more fusible than a pure silicate glass.

Like silica, boracic acid at a red heat liberates SO_3 from calcium sulphate and displaces other strong acids. Boracic acid is even stronger than silica in this respect, and so is a valuable refining agent. By producing a more fusible glass, boracic acid also facilitates the "clearing" of the molten glass. Its chief disadvantage is that it is volatile in the presence of steam and should therefore be added after all the combined water has been driven from the glass mixture, the boracic acid being added in a calcined state. Another disadvantage is the avidity with which borate glasses attack the pots or tanks in which the glass is melted, producing a turbid or seedy (p. 285) glass.

Although boracic acid in many ways behaves exactly like silica—occupying the same position in the glass molecule and even forming boric rings—it can produce an increase in hardness and fusibility similar to the effect of alkalis, this is merely a coincidence.

The low melting point of borate glasses is of great value in the production of glazes, fusible colours and enamels.

Schott's boro-flint optical glass, S_7, composed of 12 per cent. alumina, 32 per cent. lead and 56 per cent. boric oxide, contains no alkali, lime, or silica—three substances generally considered to be essential constituents of glass—and shows that the borate glasses are in several respects quite different from the silicate glasses.

Boracic acid is used in four forms: *(a)* as boracic acid, H_3BO_3, *(b)* as boric anhydride, B_2O_3 (see Vol. I., p. 355), *(c)* as crystalline borax or sodium borate,[1] $Na_2B_4O_7 \cdot 5H_2O$, or $Na_2B_4O_7 \cdot 10H_2O$, and *(d)* as calcined borax, $Na_2B_4O_7$, which may be in the form of a powder or as fragments of "borax glass." Each of these forms is equally useful though they contain widely different proportions of boracic acid. Borax cannot be used in glasses which are to be free from soda.

There is much confusion among writers on glass-making with respect to these forms of boracic acid and great care must be exercised in studying their works. Thus, it is not uncommon to see boracic acid prescribed when borax is meant, and vice versa. The water present also varies greatly and, as this is of no use in the manufacture of the glass, it is important to have the boracic acid or borax tested before use.

In small proportions, boracic acid increases the refractive index of glass, though it is much more feeble in this respect than lead oxide. Hence boracic acid or borax equivalent to $\frac{1}{50}$–$\frac{1}{20}$th of the weight of sand used in the glass mixture will appreciably increase the gloss and lustre of the glass, but it is not used for the best hollow-ware or crystal glass, as it imparts a slightly yellow tinge. Above 20 per cent. boracic acid lowers the refractive index. Contrary to potash, soda, and fluorine, the blue portion of the spectrum is reduced in glasses containing boracic acid. Lenses made of a combination of boro-flint and of phospho-crown glasses are exceptionally achromatic.

Borate glasses have a low coefficient of expansion, and so have a high thermal endurance and are very suitable for ware subject to sudden changes in temperature such as lamp chimneys and ornamental glasses decorated by fusing several glasses on each other.

Boracic acid also resembles silica in reducing the tendency of a glass to devitrify. Glasses which contain free boracic acid, or in which this is the only acid constituent, are attacked by water, so that a high proportion of boracic acid is recognised as a disadvantage. Some borate glasses are highly resistant to air, water and acids, but are strongly attacked by alkalis. Thus, a Jena Geräte glass with 15 per cent. boracic acid is specially resistant to sudden changes of temperature, and to chemicals, and Jena lamp-chimney glass with 24 per cent. is exceptionally resistant to sudden changes in temperature.

Boracic acid in coloured glasses produces brighter and more uniform colours.

Phosphoric acid, when combined with lime (as bone ash), is a well known opacifying agent, but the free acid behaves like silica, though producing glasses more readily attacked by water and so only capable of use for optical purposes.

Boro-phosphate glasses are slightly more resistant than silico-phosphate ones. A glass consisting of calcium metaphosphate with about 5 per cent. of boric oxide and 2 per cent. of silica transmits ultra-violet light.

Arsenic and **Antimonic acids** are used for two different purposes in glass-making: *(a)* as opacifying agents (p. 269) and *(b)* as refining or clarifying agents. For the latter purpose, only small proportions are used, and most of the arsenic volatilises and escapes in the manufacture of the glass.

---

[1] The first formula is that of octahedral borax, which is formed when a supersaturated solution of borax is evaporated slowly. Commercial borax is chiefly composed of $Na_2B_4O_7 \cdot 10H_2O$.

Alumina is present to a small extent in most glasses, but is introduced unavoidably as an impurity in the sand, etc., used. When added purposely, the hydrate (p. 49) is generally employed, though cryolite, $AlF_3.3NaF$ (p. 51), is used when opaque glass is desired, as it simultaneously introduces fluorine.

Alumina is a valuable constituent in many glasses, as it increases their viscosity and enables them to be worked over a longer range of temperature. It also makes glasses containing it in appreciable quantity more resistant to sudden changes in temperature, and is therefore valuable where high thermal endurance is necessary. Only a limited amount of alumina can be introduced for this purpose; if more than 3 molecules to each 36 molecules of silica are present, the excess of alumina will cause opacity by remaining uncombined. Such aluminous glasses can then be cleared by forming a glass of an entirely different chemical constitution, viz., an alumino-silicate ring compound instead of a silicate ring compound with alumina in the side chain position. Such alumino-silicates do not, however, make good technical glasses, though invaluable in the form of glazes for bricks, tiles, and pottery.

Cullet is broken glass, and is usually added to a mixture of raw material as a means of using up scrap glass, and also to start the reaction between the other materials.

Chemical reactions depend for their intensity on the intimacy of the contact between the reacting substances. This is increased when the reaction occurs in a fluid medium, and the use of cullet (which melts before the reaction of the other materials has proceeded very far) facilitates the production of the glass by providing a medium in which the combination of the silica with the various bases may occur.

Some manufacturers of bottles use nothing but cullet of flint glass which they collect from various dealers.

Mixed cullet (*i.e.*, cullet composed of several different kinds of glass) is almost useless, especially if it contains much common bottle glass, but cullet from works making only high-class glasses is a valuable material.

Decolorants are substances added to glass in order to remove an objectionable colour which it would otherwise possess. Thus, iron gives a green or brown colour, which can be removed by the addition of **manganese dioxide.**

Normally, iron gives a greenish shade, but this becomes yellow or brown on account of the oxidising action of the manganese on the iron. Any oxidant of sufficient power would do equally well, but manganese dioxide has an additional advantage inasmuch as it gives a slight pink tinge to the glass, and as this pink is complementary to the yellow colour of the iron compound, the two colours neutralise one another, and a whiter glass is produced.

Only about 10 per cent. of the manganese dioxide added to the glass acts as a decolorant; the remainder forms colourless silicates and is wasted. There is, consequently, room for great improvement in this direction—possibly by the substitution of another more stable compound of manganese.

In flint glasses the **red lead** and **nitre** are both oxidants, and so act as decolorants of the iron compounds. **Nickel compounds** form reddish glasses and thus act as decolorants where the proportion of iron is only small, as in plate and mirror glasses. **Selenium compounds** have been extensively used during recent years as decolorants by forming pinkish glasses, and in addition to this they also improve the lustre of the glasses to which they are added. Arsenic acid, As_2O_5, is also useful as a decolorant in certain glasses.

Colouring agents are used in the manufacture of opaque and coloured glasses. The latter are considered separately on p. 294.

TECHNICAL CLASSIFICATION OF GLASSES

The glasses of chief importance may conveniently be classified as follows:—

I. **Crown glasses,**[1] composed of soda, lime and sand, but with a composition varying according to the oxides which are used to replace those mentioned. Thus potash may replace the soda in whole or in part, and baryta may replace a portion of the lime. Crown glasses are used for a variety of purposes, and specially for sheet glass, plate glass, and for optical work.

II. **Bohemian glasses,** composed of potash, lime and sand, or quartz, used chiefly for hollow-ware.

III. **Flint glasses** or **lead glasses,** composed of potash, red lead and sand, used for hollow-ware, bottles of superior quality, and for optical work. These glasses are known in France as **cristal.**

Where sand of sufficient purity is difficult to obtain, flints crushed to fine powder may be used instead, but such glasses ought not to be known as flint glass.

IV. **Bottle glasses,** usually composed of soda, lime, alumina and sand, the latter being less pure for the commoner bottles.

The alumina is seldom added separately, but is a useful constituent of the sand employed.

V. **Boro-silicate crown glasses** resemble crown glasses, but part of the silica is replaced by boric acid, so as to confer special properties. These glasses are chiefly used for optical purposes, laboratory ware, and for thermometers.

VI. **Boro-silicate flint glasses** resemble flint glasses, but part of the silica is replaced by boric acid. These glasses are chiefly used for optical work, enamelling, and for artificial gems.

VII. **Phosphate glasses** may be of either the crown or flint type in which part of the silica has been replaced by phosphoric acid. They are used almost exclusively for optical purposes.

VIII. **Silica-free glasses** are those in which the whole of the silica is replaced by boric or phosphoric acid. They are so costly as only to be suitable for special optical purposes.

IX. **Water-glass** and other simple silicates are not usually included among the glasses, as they are unsuitable for the technical purposes for which glasses are used. For **Water-Glass,** see p. 142.

X. **Opaque and coloured glasses** are made from the glasses mentioned above by the addition of opacifying or colouring agents (see also p. 264).

Glasses are also classified according to the processes used in their manufacture or working; thus **blown glass** is that which can be shaped by the pressure of the human breath, applied by means of a blowpipe or pontil; **plate glass** is that which is capable of being rolled into a plate or sheet; **sheet glass** is that which can first be blown into cylinders, and then flattened into a sheet; **table glass**[2] is that which is specially suitable (on account of its brilliancy) for the manufacture of hollow-ware for table use.

---

[1] The term "crown glass" should, strictly, be applied to glass articles produced in a special manner (p. 285), but it is also largely used as the name of a type of glass, as indicated in the text.

[2] In reading German books on glass manufacture (and some translations of them) it is important to remember that the word **Tafelglas** does not mean "table glass," but plate or sheet glass.

For **hollow-ware,** a light flint glass is generally used on account of its lustre and brilliant appearance. It is sometimes parti-coloured by flashing, that is by gathering a little glass of another colour on the outside of the main piece of glass, and working the two together. Machines normally work crown or bohemian glasses.

If the ware is to be moulded, it must be plastic over only a short range of temperature; this is attained by the use of a small proportion of alkali, or by using a mixture of soda and potash instead of one of them, in an alkali-lime (crown) glass, and keeping the lime as low as possible.

In **bottle glass,** cheapness, strength, and resistance to the fluids likely to be used are the chief desiderata, and they are usually secured by the employment of glasses low in alkali, high in metals of the RO group, and with alumina up to 10 per cent. A considerable proportion of iron is no objection in bottles used for many purposes, especially as it provides a coloured glass without extra cost. A low alkali content is specially necessary in glasses which are blown mechanically.

Glass used for the manufacture of bottles containing fermented liquors must be resistant to the action of such liquors and the gases produced during fermentation. Champagne bottles must be very strong as the pressure of the gas produced sometimes reaches five atmospheres.

Colour being of minor importance, much interest is taken in the numerous attempts which have been made to use the **slag from blast furnaces** as one of the principal ingredients of a bottle glass. By placing a glass tank, heated by a Siemen's regenerative furnace, close to the blast furnace, and allowing the molten slag to run direct into this tank, more than half the material necessary for the glass is obtained in a molten state. The addition of a suitable quantity of soda and sand will produce a glass of a quality quite good enough for common bottles, and a few works are using this method satisfactorily. The great drawback is the necessity of the glass-blowers being subsidiary to the men working the furnaces, and the large amount of slag wasted, because the glass is not made and used as fast as the slag is produced. There is, however, room for further work in this direction as a good means of disposing of blast-furnace slag in a hot state is a great desideratum.

Bead glass is not a special variety of glass, though it is stated to be so in some books.

The glass is usually a crown glass to which a little alumina has been added (in the form of impure sand), and the beads are made by drawing tubes, chopping these into small pieces, and rounding the edges by placing the pieces on a tray and heating them to redness in a furnace.

MIXING AND PREPARING THE BATCH

In order to obtain the best results it is essential that the composition of the mixture or **batch** and the conditions under which it is heated shall be as uniform as possible.

Glass manufacturers are, therefore, loth to change either their furnaces or their fuel, and adhere as closely as possible to one source of supply for each of their raw materials. With improved methods of analysis and of testing raw materials, it is now possible to cheapen the cost of production by providing a wider range of ingredients; but the serious results which may follow a mistake in the proportions, or in the nature of any of the materials used, are sufficiently important to prevent some manufacturers from availing themselves of the best scientific information on the subject. The larger manufacturers do not hesitate to apply modern scientific methods, including statistical analysis of all variables leading to losses, and a well-equipped laboratory is now considered an essential part of the factory. This has led to a wide range of special purpose glasses being developed in recent years. (See Table, p. 264.)

The **proportions** of the various ingredients cannot be determined entirely from the composition of the finished glass, owing to the loss of material in the form of scum (known technically as **sandiver**[1] or **glass gall**), and to the loss of alkali, etc., by volatilisation. Moreover, the yield of the definite compound which is the essential constituent of the glass is not perfect, and small, but varying, proportions of other compounds are formed and included in the material of the glass. The following **recipes** are fairly representative of the glasses mentioned, but it must be understood that each glass maker has his own recipes, based on the materials and conditions to which he is accustomed. Moreover, each different sand requires some modification in the composition of the batch, so that recipes can only be indicative of the proportions used, and can seldom be followed implicitly:—

Crown Glass.—Sand, 100 parts; chalk, 24 parts; sodium sulphate, 50 parts; charcoal, 4 parts; cullet (broken glass), 200 parts.

Window Glass.[2]—Sand, 100 parts; chalk, 28 parts; sodium sulphate, 42 parts; cullet, 100 parts; arsenic acid, 1 part; charcoal, 3 parts; manganese dioxide, ½ part.

Plate Glass.—Sand, 100 parts; chalk, 30 parts; sodium carbonate, 32 parts; potassium carbonate, 6 parts; cullet, 100 parts; manganese dioxide, ½ part; nitre, 2 parts.

Flint Glass or Crystal.—Sand, 100 parts; potassium carbonate, 33 parts; red lead, 67 parts; manganese dioxide, ½ part; potassium nitrate, 7 parts; cullet, 100 parts.

Baryta Glass.—Sand, 100 parts; sodium carbonate, 30 parts; barium carbonate, 90 parts; red lead, 65 parts.

Bottle Glass (Green).—Sand, 100 parts; sodium sulphate, 38 parts; chalk, 33 parts; charcoal, 2 parts; manganese dioxide, ½ part; cullet, 50 parts.

Bottle Glass (Brown).—Sand, 100 parts; sodium sulphate, 35 parts; chalk, 34 parts; cryolite, 10 parts; charcoal, 2 parts; manganese dioxide, 8 parts; cullet, 50 parts.

The following recipes were published in 1915 by the Institute of Chemistry as the result of an investigation, made under the auspices of that body, into the best methods of producing glasses in Great Britain to replace those previously imported from Germany:—

	1	2	3	4	5	6	7	8	9	10	11
Sand - - - -	67.0	67.0	67.0	68.2	68.2	65.0	65.0	65.5	72.0	68.0	68.0
Alumina - - - -	6.5	8.3	10.0	6.2	6.2	1.0	1.0	2.5	10.0	4.0	4.0
Sodium carbonate - -	34.2	29.0	17.0	5.5	5.5	14.0	...	10.2	11.2	26.0	26.0
Calcium carbonate - -	11.6	9.6	12.5	13.0	14.2	0.6	0.6	...	11.0	12.8	12.8
Calcium fluoride - -	...	1.6	...	1.0	...	...	...	...	...	...	...
Barium carbonate - -	...	...	...	8.8	8.8	...	...	...	...	...	...
Magnesia - - - -	...	...	0.5	...	...	...	...	5.0	0.5	...	...
Potassium nitrate - -	...	...	1.0	4.3	4.3	3.0	3.0	...	3.0	14.5	...
Borax (anhydrous) - -	...	..	...	...	...	...	26.68	13.0	7.2	...	...
Boric anhydride - -	...	2.0	8.0	5.5	5.5	24.0	5.5	...	...	...	...
Antimony oxide - -	...	...	...	...	...	1.0	1.0	...	...	...	...
Arsenious oxide - -	...	...	..	...	...	2.0	2.0	...	...	...	...
Zinc oxide - - -	...	...	...	...	...	...	...	8.0	...	...	..
Potassium carbonate -	...	...	...	...	...	...	...	...	...	...	[illegible]

---

[1] It is composed almost exclusively of calcium and sodium sulphates, with about one-tenth its weight of glass.

[2] Window glass is also known as **sheet glass.**

1 is a soft glass, not readily soluble or easily devitrified, and works well in the blowpipe.

2 is a soft glass of higher quality.

3 is a glass suitable for pharmaceutical purposes; it is highly resistant to chemical action, withstands changes of temperature well, and should be a very suitable glass for high class beakers, flasks, etc.

4 and 5 closely resemble Jena combustion tubing.

6 and 7 are glasses for miners' lamps, and withstand rapid changes in temperature.

8 is a glass almost identical in its general behaviour with Jena resistance glass; withstands changes of temperature well, but, like Jena, is not suitable for working before the blowpipe without oxygen enrichment. It darkens and tends to devitrify; operations—such, for instance, as sealing side tubes into flasks—are difficult, if permanent and neat joints are required. For some purposes, No. 3 may be substituted as it works well in the blowpipe and is highly resistant chemically.

9 is an alternative mixture for combustion tubing, and does not become cloudy so readily as Nos. 4 and 5.

10 and 11 are soft glasses specially suitable for tubing and X-ray bulbs. 10 being the better of the two, when used for X-ray bulbs, gives a blue phosphorescent glow; if a green glow is desired, a little manganese dioxide should be added to the batch mixture.

It is essential that all the materials should be finely ground before weighing. They should be weighed as accurately as possible, and then mixed by means of a wooden shovel, or preferably in a mixing machine, so as to secure as uniform a product as possible. The batch or mixture is then placed in the hot pots or pans in small quantities at a time until the vessels are almost full of molten material. The actual melting usually occupies ten to twelve hours, but depends on the quantity to be made and on the type of furnace used. There is a large evolution of gases during this operation, and these form a froth or scum which must, from time to time, be ladled from the surface. Fire-clay rings are placed on top of the molten glass or **metal** when open pots are used, these rings serving to collect the scum or gall, and facilitating the operation of clearing the surface of the glass.

When the frothing has ceased and the scum has been removed, the glass must be refined or **planed.** This may be accomplished in various ways: one consists in throwing in potatoes or apples, or stirring with a strip of green wood so as to effect a reduction of any matter which may be removed in this manner, and also to produce a further volume of gas which will help in the stirring of the molten glass.[1] The usual method of planing, however, consists in stirring the glass with a fire-clay cylinder attached to a long iron rod. During the refining process it is necessary that the glass should be very intensely heated, so that it is very fluid and mobile; its temperature sinks gradually during the stirring, and towards the end of the process the glass is quite viscous. The glass-maker draws trials or test portions from the furnace and examines these; when they show that the glass is clear and can readily be drawn into long threads, the stirring is stopped, and the glass is allowed to cool still further until it is sufficiently viscous for use.

If one "planing" is insufficient it must be repeated as often as may be necessary. Three such treatments will usually suffice if the glass has been rapidly melted, and is sufficiently fluid. The use of a recording pyrometer (Vol. I., p. 533) to ascertain the temperature of the glass is advantageous.

It is generally thought that the stirring of the glass is a purely mechanical means of securing uniformity, but Zulkowski has carried out experiments which seem to show that the intense heating, followed by prolonged stirring, are the means of effecting chemical changes within the molten mass, and that without this treatment the substances which form the essential constituents of the glass are not produced.

---

[1] In some works the potatoes or apples are inserted on the pointed end of an iron rod, which is then used to stir the glass.

The melting of optical and of most other special glasses is effected in closed pots, the stirring of which is difficult and sometimes impossible. Such glasses must therefore be broken up, and the cleanest fragments selected and remelted, in order to obtain the best results.

The vessels in which glasses are melted are of several types. Where large quantities of glass are manufactured, open tanks are used, but for special glasses, or those which require to be kept particularly clean, pots (Figs. 6 and 7) are employed. Where it is particularly necessary to prevent portions of the brickwork from the top of the furnace, or other extraneous matters, from falling into the glass, the pots are provided with tops, and the glass is withdrawn through small openings at the side. Both tanks and pots are made of fire-clay of the best quality. They require great skill in their manufacture, especially the larger ones, which hold 12–18 cwt. of glass. They must be annealed carefully before use, and when once heated they must never be allowed to become quite cold again. With careful use a glass pot will last three months or more,[1] but sometimes a pot will break after two or three days' use. Some pots have a vertical partition, so that the scum is automatically separated.

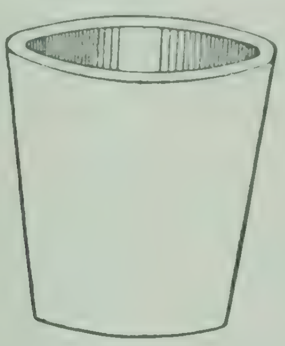


FIG. 6.—Open Glass Pot.

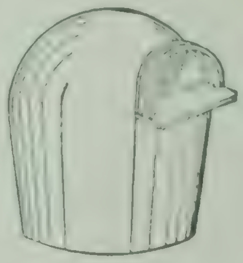


FIG. 7.—Covered Glass Pot.

The use of direct, coal-fired furnaces for heating the pots or tanks is diminishing, as gas-firing is more economical and more satisfactory. Several pots are usually heated simultaneously.

Producer-gas is used, and the main feature of the furnaces is the employment of a regenerator of the type devised by Siemens (see Vol. I., pp. 126 and 572). This regenerator consists of a series of passages filled with checkered brickwork through which (*a*) the products of combustion and (*b*) fresh air for burning the fuel pass in opposite directions. In the regenerator, the outgoing gases heat up one series of bricked chambers, and, by changing a valve, the gases are turned into another set of chambers, the ones previously heated being then used to warm the incoming air required by the furnace. By this means an intense heat is obtainable without using an exorbitant amount of fuel.

For heating small quantities of special glasses, wood is superior to coal, and for many years was the only fuel used in glass-making. The improvements effected in gas fired furnaces during recent years have now, however, resulted in the disuse of wood except in a very few instances.

In a glass tank-furnace arranged for a continuous supply of glass, it is necessary to secure: (i) complete and rapid fusion of the glass mixture; (ii) a suitable rate of charge and discharge; (iii) the withdrawal of the molten glass before it has been overheated and so begun to devitrify. The chief drawback of a continuous furnace is the glass-gall produced by the sodium sulphate (Glauber salt), which floats on the surface of the molten glass, spoiling it and corroding the sides of the tank very rapidly. Tanks having two or more compartments are not durable, as the partitions are rapidly corroded.

---

[1] When special skill and care are exercised in the manufacture and use of glass pots, they may last a year or more. There is ample scope for a full investigation of glass house pots; at the time of writing those having the longest "life" are made in the United States.

Several attempts have been made in the past to utilise **electric furnaces** for glass-making, with a fair amount of success. The two most successful types of furnace for this purpose are the **Voelker** (Fig. 8), and the **Becker** (Fig. 9), respectively. In each case the batch mixture flows between rows of carbons which convey the electric current, and the glass, as it melts, flows into a lower receptacle. Scumming is avoided by the use of baffles. For bottle, sheet, and plate glass these furnaces have proved quite satisfactory, but some users complain of difficulty in obtaining a sufficiently homogeneous glass. Electric furnaces do not appear to be well adapted for optical glass, and as they have not proved cheaper than gas-fired furnaces of the tank type in localities where coal is not above the normal price, the field of usefulness appears to be limited to those places where water-power or other special facilities suggest the preference for electricity as a source of heat. This explains their utilisation in France and Switzerland.

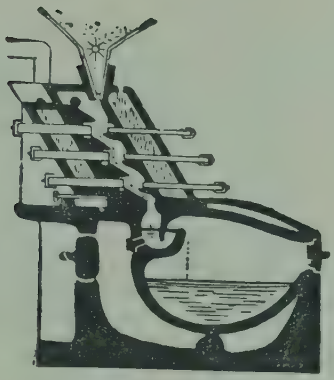


Fig. 8.—Diagrammatic Section of Voelker's Electric Furnace.

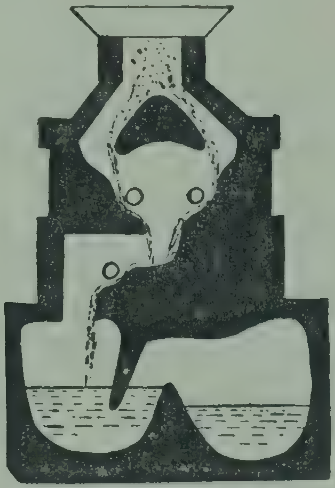


Fig. 9.—Diagranmatic Section of Becker's Electric Furnace.

GLASS-WORKING

Various methods are employed in making articles of glass, but the majority of them are based on the production of a hollow flask by **blowing** (blown glass), or on the production of a plate made by **casting** the glass and then **rolling** it. What is known as **pressing** is the use of moulds as a means of forming the outer shape of the article; it may be employed in combination with either casting or blowing.

The **blowing** of glass not only requires the possession of much strength and good lungs, but also a considerable amount of dexterity and skill, particularly for some of the more elaborate and delicate wares. The chief tools required are a pontil or iron (Fig. 10), which consists of a pipe some 5 ft. in length, and a number of tongs, shears, and other simple tools. The workman dips one end of his pontil into the viscous glass in the furnace, and withdraws it with a suitable quantity of glass on the end. Some skill is required in "gathering" the correct amount of glass, and in coiling it round the end of the pipe in the position desired. The men work in gangs of four, as a considerable amount of assistance is required in some of the operations. Boy labour is increasingly used in many of the works.

Two systems of working are in use. In the **old** one the glass on the end of the pontil is rolled on a polished iron plate or **marver**, and is then slightly hollowed by blowing. Its shape is regulated by a continuation of the blowing, accompanied by a swinging motion of the pipe, and, frequently, by the use of small iron tongs (Fig. 11). Accuracy in shaping is dependent almost entirely on the skill of the workman, and it is precisely because of the difficulty in obtaining sufficiently skilled men that this method of working is falling into disuse where many articles of the same shape are to be made. In the case of a wine glass, the bowl is shaped as just described, and the leg is made by pulling out the thickened mass at the end of the bowl, or by attaching a fresh piece of glass to the bowl and pulling this out to the desired shape. Meanwhile an assistant has been blowing a separate piece of glass, at the same time twirling his pipe rapidly, so as to cause the glass to move centrifugally and produce a flattish disc instead of a spherical bulb. This disc is then heated momentarily in the furnace, and is then attached to the leg of the wine-glass on the first pontil, so as to form the foot of the glass. Some men prefer to attach the foot when it is in the shape of a bulb, and to rotate it to shape after breaking it off the pontil to which it was first attached. When this is done, the glass must be cut from its original pontil and mounted, by means of its foot, on a second pipe. The mouth of the glass is then trimmed smooth and even with shears, and by holding it in the mouth of the furnace its final shape can be given by means of a tool resembling a large pair of sugar tongs.

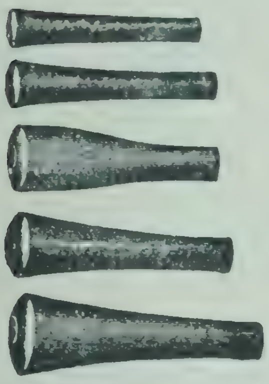


FIG. 10.—Ends of Pontils.

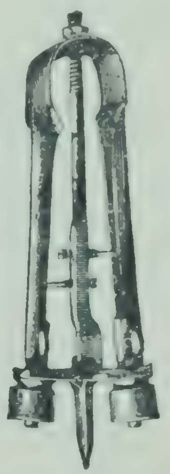
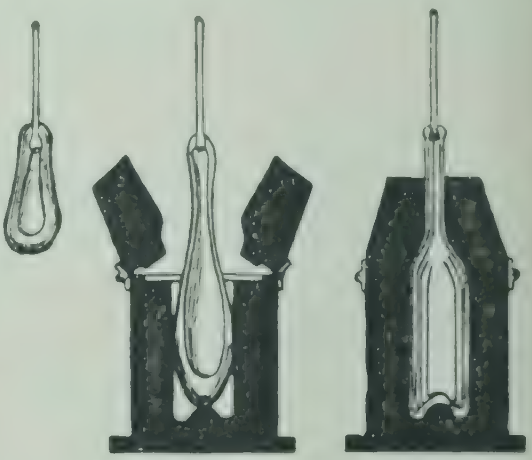


FIG. 11.—Tongs for Trimming Glass.



a *b* *c*

FIG. 12.—Three Stages in Moulding a Bottle.

The foregoing system is the one by means of which the beautiful glass ware of ancient times was made. It is, however, slow and requires an enormous amount of skill, so that for many purposes it has been replaced by a method in which the shape of the vessel is given by means of a mould. The use of this mould reduces the amount of skill required, it increases the speed at which the men can work, and it ensures all the vessels being of the same shape and size.

The **new** method is illustrated in Fig. 12. The mass of glass is gathered on the pontil and rolled on the marver as before, but instead of being blown to shape, it is placed inside an iron mould and then blown. The mould prevents the glass from taking any other shape than that intended, and greatly facilitates the working. The mould is lubricated by means of a splinter of wood which is ignited by the hot glass,[1] and by revolving the pontil all seam-marks in the mould are prevented from being transferred to the glass. In the case of bottles, the neck is usually finished by means of a pair of tongs, the ends of which form a supplementary mould. This is considered to be more convenient than the use of a larger mould which forms the neck at the same time as the bottle, and is certainly much cheaper, as one pair of tongs will serve for several moulds. Where long-necked bottles are desired, the mould must be supplemented by a second (Fig. 12, *b*), as otherwise it would be difficult to withdraw the bottle from the mould. In the case of a wine-glass made by this system, the bowl is shaped by means of the mould, the leg is made as on the old system, and the foot attached in the same manner. The glass is then cut off the pontil and sent to the annealing lehr. The mouth is finished in the annealed glass, by cutting and grinding, instead of working the glass in a viscous state at the furnace. Handles and decorative work, such as threads or beads, must be applied to the hot glass, and such articles are, therefore, best made by the old system, as the glass is cooled by the mould and is difficult to heat again without risk of devitrification. Much skill is shown in the way some glasses have been decorated by simultaneously gathering two or more kinds of glass on the pontil and then proceeding with the working. In this way, elaborated coils and other designs are made in a comparatively simple manner.

---

[1] A better lubrication is secured by painting the inside of the mould with a pasty mixture of pitch, wax and sawdust, and then heating the mould in a furnace until the lining is carbonised. Cast-iron moulds may be lubricated with graphite and a binder in a suitable vehicle.

Combinations of both the old and new methods are largely in use. Thus, in some works instead of using the marver, the bulb of glass is shaped by pressing it on a wet wooden dish. Wooden tongs for flattening the feet of wine-glasses and other simple tools are much more extensively used than formerly.

The enormous demand for cheap bottles has resulted in the invention of numerous machines in which the process of blowing and pressing may be effected mechanically. The machine which has gained the most recognition is that patented by **Owens** in 1905 in America, and controlled by the European Glass Bottle Syndicate. The early machines, with the aid of six men, produced no less than 15,000 to 20,000 bottles a day, whereas a skilled blower will not make more than 350, and few men will exceed 300 bottles in the same time.

The machine is too complex to be described in detail, but briefly it consists of six horizontal arms on a vertical rotating shaft, each arm being fitted with a blast and suction device, so that each arm produces a complete bottle with every revolution of the shaft. When the machine is at work, an arm, carrying a mould, dips the latter into the glass tank, and simultaneously exhausts the air from the mould, thereby filling it with glass. The arm is then raised and moved away from the glass tank, during which motion the suction is stopped, any excess of glass is cut off automatically, and the mould is then removed, leaving the glass hanging from the arm in the shape of a bulb. A new mould is now placed around the glass, and the air blast is turned on so as to make the glass into the required shape, after which the mould and bottle are both removed, and the arm is lowered and ready to commence the making of a new bottle. The bottles must be dressed and freed from sharp edges, particularly at the neck. This is effected by the same machine, which carries the bottles round to a small furnace and holds them in such a manner that the edges are rounded by the heat; they are then sent to the annealing chamber. The glass tank containing the molten glass is preferably made to rotate, so that the cold arm does not always dip into the same part of the tank and so chill the glass unduly. Frequent changes of moulds are necessary, and a fitter must be employed to keep the machine in order, otherwise all the men employed may be unskilled as the machine is almost automatic.

Glass of the ordinary composition may be used with this machine, but it is desirable to replace the greater part of sodium sulphate by a corresponding proportion of sodium carbonate. Felspar should be absent, and the glass must be heated sufficiently to make it properly fluid.

The **Brühler machine** for wide-mouthed bottles, tumblers, etc. is illustrated in Fig. 13.

The development period of the hand-operated bottle machine in America (U.S.A.) was from 1898, of the Owens automatic machine from 1905 to 1917, and of the flow-feed devices from 1917 to 1924.

The rights of the Owens machine were originally offered to British manufacturers for £600,000, and were eventually bought by bottle-makers from seven European countries, including Britain, in 1908.

By 1924 the change-over from hand-blowing to automatic production in Lancashire was substantially complete; the percentage of jars and bottles made on automatics rising from 50 in 1917 (the year the first machine—an O'Neill—was operated) to 90 in 1924.

In the six years from 1924 to 1930 the consumption of bottles and jars increased by 13 per cent. by weight but decreased by 16.8 per cent. in cost (17/3^d and 14/4^d per cwt. respectively).

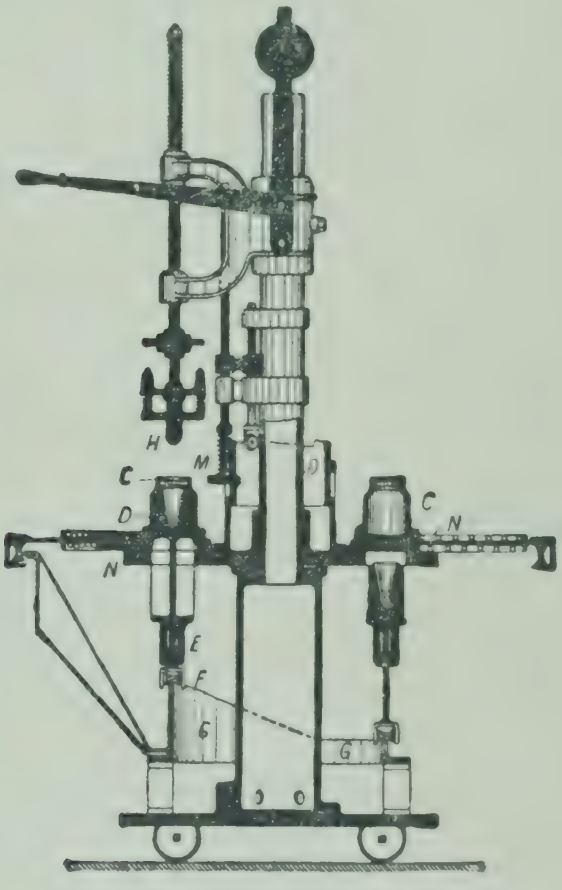


FIG. 13.—Brühler's Glass Machine.

For small works the Roirant machine has recently been developed with one to six arms. The six-arm machine produces 33,000 litre bottles per 24 hours. Each arm may produce a different size or shape of article. Both the Owens and the Roirant machines work from a rotating working-end in the tanks.

The modern ten-arm Owens machine produces about 43,000 litre bottles in 24 hours, the six-arm Roirant machine type A6 about 19,000.

In 1942 about 40 Owens machines and 60 Roirant machines were working in Germany.

Sheet glass was formerly made by blowing a bulb on the end of a blowing iron, flattening it until its diameter was sufficiently large, then again blowing it until a long bulb, whose sides were the same thickness as that of the desired sheet, was obtained. The solid end of this bulb was then cut off with a cold iron, and the mouth widened into a cylinder by means of a pair of spring tongs, the glass being meanwhile rotated somewhat rapidly. The open end of the cylinder was next received on a pontil with an enlarged end, and attached to it by means of three small pieces of semi-molten glass. The blowing rod was then cut off and the other end enlarged into a cylinder by means of the spring tongs. The cylinder was then slit lengthwise and placed on a hot fire-clay slab, a polishing iron was then placed inside it, and rolled backwards and forwards so as to flatten the cylinder into a sheet. For this purpose the fire-clay slab must be kept sufficiently hot to soften the glass, but not hot enough to melt it. The various stages of blowing and making into a sheet are clearly shown in Fig. 14.

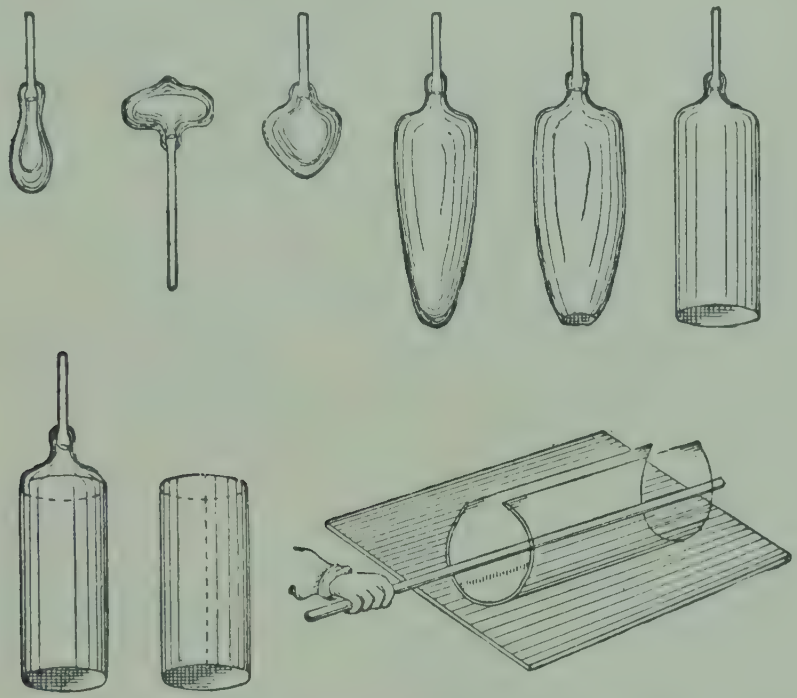


FIG. 14.—Nine Stages in Making a Sheet of Glass.

For sheets 4 ft. to 6 ft. in length the use of the lungs alone will not provide sufficient air, so that compressed air was supplied to the blowing iron.

Various mechanical methods of making sheet glass have been devised, and are now responsible for the bulk of the sheet glass produced.

Drawn Sheet Glass.—In the Libbey-Owens machine (Fig. 15) a wide band of molten glass drawn up from the tank is allowed to bend over an air-cooled roller before passing, on further rollers, through an annealing tunnel. Here the temperature is allowed to fall at a predetermined rate from about 700°–800° C. to a temperature at which the glass can be handled. On emerging, it is cut into suitable lengths. By adjusting the speed of operating, glass of any thickness between 0.6 mm. and 7.0 mm. can be obtained in a width of 8 ft. 6 in. Two machines are usually fed from one tank. The Foucault process is illustrated in Fig. 16.

Continuous glass tanks are provided with 3 to 5 firing ports on each side. They may be 25–30 m. long, 4–6 m. wide and are capable of dealing with one ton of glass per sq. m. melting surface in 24 hours (160 t./24 hours for a surface of 156 sq. m. at the Skoda works). Over a year's continuous working is not unusual with fused alumina refractory blocks in the tank walls.

Large vessels, such as carboys for the storage of acids, are blown by means of human lungs for the first stage, and afterwards a little water is introduced; this is rapidly converted into steam, and secures the expansion of the glass to the desired size.

Sievert & Co., Dresden, have produced numerous articles by casting a slab of glass on a perforated plate, clamping it down thereon, inverting the plate so that the glass hangs suspended above a mould, and then forcing compressed air through the perforated plate so that the glass is blown to fill the mould.

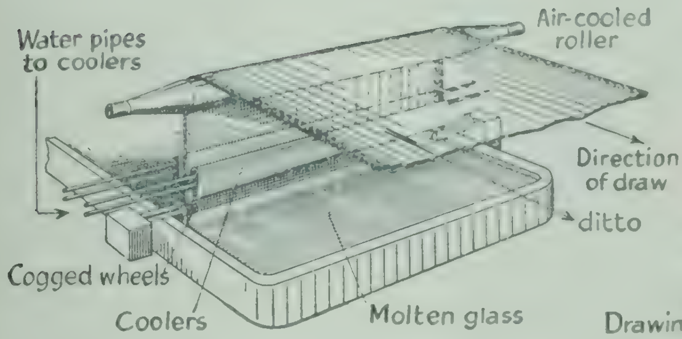


FIG. 15.—Libbey-Owens Process.
(*Courtesy, Deutsche Libbey-Owens Gesellschaft.*)

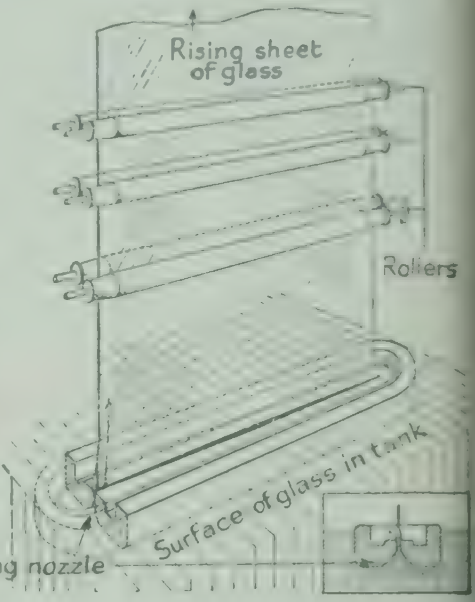


FIG. 16.—Foucault Process.

This arrangement enables large tanks for electric accumulators and other purposes to be made very cheaply. A modification of this arrangement is also used for the manufacture of large cylinders and for sheet glass.

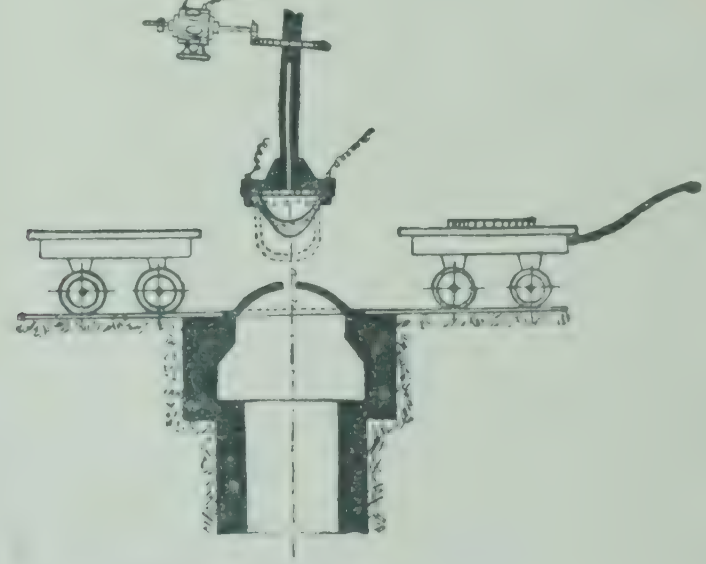


FIG. 17.—Sievert's Process.

The arrangement was originally patented in 1904, but has since been improved in several respects. The form in which it is at present used by Engels & Cie, Film, is shown diagrammatically in Fig. 17. A steel ring, fitted with a rabbeted edge, is laid on a waggon and is filled with molten glass. As soon as this glass has become sufficiently tough the waggon is moved until the ring is exactly under the hollow shaft. The latter is then lowered until its base touches the ring. An electric current is then applied to the base, and the latter is converted into a powerful magnet, so that when the shaft is raised to the position shown in Fig. 17, the ring is lifted with it. The waggon is now removed, the shaft is lowered into the mouth of the furnace so as to warm the glass thoroughly. The shaft is again raised, a fresh waggon placed beneath it, and air is blown through the hollow shaft whilst it is rotated rapidly. This causes the glass to expand uniformly to the shapes indicated, and when the blowing is complete the shaft is lowered so that the glass rests on the car. The electric current is then cut off, and the glass is thereby freed from the shaft and can be carried away, or the ring can be held by a separate carrier and the glass allowed to remain suspended. Cylinders of large size can be produced in this way much more rapidly than by hand blowing.

Crown sheet is one of the oldest methods of making sheet glass, but is now seldom used except for special purposes, such as the manufacture of microscope slide covers. It requires a glass of considerable toughness and fluidity.

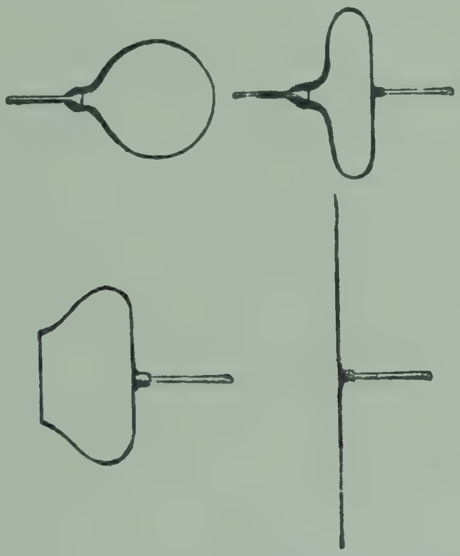


Fig. 18.—Four Stages in the Manufacture of Crown Sheet Glass.

A ball is first blown (Fig. 18) and then flattened on the marver; a pontil or rod is then fastened to the centre of the flattened portion of the glass, and the blowing iron is cut off. The glass is warmed again and is then revolved rapidly on the pontil, so that under the influence of centrifugal action the glass spreads and ultimately forms a flat sheet, with a "bull's eye" in the centre. This method is costly, and has been replaced by the use of modern machines.

Fluted sheet glass is made by blowing the bulb into a mould, the walls of which correspond to the desired flutes. Other patterns may be made in the same way, but it is better to use the process employed for plate glass.

Defects in sheet glass are comprised under four heads: **seediness** when the glass is contaminated with bubbles owing to its not having been properly refined; **stones** or uncombined particles which may be seen on examining the glass with a lens; **colour** due to some impurity in the sand (see "Coloured Glasses," p. 294), or to an insufficient or inaccurate application of a decolorant (p. 273); **stringiness** or **striæ**—wavy and irregular markings in the glass, due to its irregular expansion during blowing or flattening, or to its not having been heated sufficiently during manufacture. Other defects are described on p. 293.

The **casting** of glass is chiefly used for two purposes: (a) the direct moulding of thick dishes, basins, and other simple objects, and (b) in the manufacture of plate glass.

Plate glass is chiefly used for large windows and mirrors. It is clearer and more transparent than sheet glass manufactured by blowing, but it is more costly. The present method of making plate glass does not differ materially from that used for over two hundred years; the chief improvements have been in means whereby plates of very large size may be produced.

Modern machine-made sheet glass is of such high quality that it is often supplied as "plate," for instance, for cheap mirrors. Genuine plate glass is polished on both sides by means of abrasive powders, of which sand is the cheapest and most widely used, followed by polishing powders such as rouge. The individually cast plate ground and polished, first on one side, then on the other, is gradually being superseded by continuously drawn sheet ground and polished on both sides at once. A continuous sheet 6 ft. wide and up to 400 ft. long may be dealt with in such a machine.

The molten glass in a suitable melting pot is slung over the casting table by means of a crane, and its contents are poured out as evenly as possible on an iron table. An iron roller is then rolled across the viscous glass, reducing it to a uniform thickness throughout. The thickness is determined by two straight-edges placed one on each side of the table at a distance depending upon the desired width of the plate. The glass plate is then taken to the annealing oven, and is afterwards levelled and polished. The casting table must be of stout metal or it will warp and twist under the influence of the heat. The roller is better if heated internally, though many works do not adopt this precaution.

When the cast and rolled plate is removed from the annealing chamber it has a rough, opaque, and undulating surface, but the interior should be quite clear. The plate is examined as to its freedom from defects, trimmed to shape and sent to be ground.

The glass is fastened to a grinding table with plaster of Paris, and the table is rotated at about 30 revs. per minute. Two or more ribbed rollers run eccentrically over the surface of the glass, their action being aided by the use of wet sand or emery. The final polish is given with felt and leather rollers and rouge. The polished plate is then cut into pieces by means of diamonds (small steel wheels are now used as a substitute). If bent sheets of plate glass are required for curved windows, etc., the polished plate is bent by heating it in iron moulds of the desired shape.

Small pieces of plate glass are usually rolled by means of a loose hand-driven roller, but for the larger sheets the roller is worked mechanically.

The grinding and polishing removes about half the thickness of the original plate, and as the glass removed is in the form of fine powder mixed with sand or rouge it represents a serious loss. Various attempts have been made to recover the glass from the waste abrasives, but without much success. A further loss is caused by the volatilisation of a large proportion of the soda from the tank in the original melting process.

Reinforced glass consists of plate glass in which wire netting is embedded. The glass is cast, and is treated by three rollers, the first of which spreads it into a sheet; the wire is laid over this and is embedded by the second roller, after which the third roller covers the wire with a film of glass and rolls the whole together.

The wire prevents the glass from falling, even when the latter is broken, and affords a good protection against stones and other missiles. It also enables the glass to afford a greater protection in case of fire or burglary.

For **figured plate** a pattern is cut on the bed or roller, and this is automatically transferred to the glass.

Patent plate is sheet glass manufactured in the ordinary way, but afterwards polished so as to remove the striæ which usually disfigure it slightly.

Pressed glass may be made in two ways: (*a*) the glass may be gathered on a pontil, placed in a mould and blown to shape as described on p. 279, or (*b*) the viscous glass may be dropped into a mould and squeezed to the desired shape by means of a plunger as in the Brühler machine (p. 281). Great accuracy is required to allow just the requisite quantity of glass to enter the mould. The hot article may be fire-polished by exposing it to the heat of a suitable blast burner, after which it must be annealed.

Annealing or cooling the hot glass under suitable conditions is an essential part of the process of manufacture, as glass which has been cooled too quickly is unstable, and may fall to pieces at any moment. As soon as possible after the article has been made it is, therefore, sent to the annealing chamber.

Two patterns of these are in use: in one the temperature of the oven is raised so as to be close to that of the glass placed in it, and it is then allowed to cool very slowly. In the other method of annealing, the goods are placed at one end of a tunnel or **lehr** and pass slowly through it until they reach the other end, when they are removed in an annealed condition. This is a more rapid and satisfactory method of annealing, and the temperature is under more complete control. It will, therefore, come into increased use in the course of time. Where glass is blown mechanically the output necessitates a lehr of large capacity, or some method whereby no time is lost in the process of annealing. For many purposes, the best form of annealing oven is a tunnel 90 ft. long by 6 ft. wide, with an endless band running through it. The bottles or other articles are placed on this band and travel through the oven in an automatic manner, the short time for correct annealing in such a lehr being surprising to those who are accustomed to the older type of cooling oven. Indeed, the introduction of large tanks for melting the glass (as in Siemens' regenerative furnace and its modifications), combined with the use of mechanical blowing and moulding machines, would have been useless had it not been for the almost simultaneous invention of the tunnel annealing chamber.

Hardened glass is that which has been cooled very rapidly, so as to produce an exceptionally hard surface (see p. 267), but no method has been found which is completely satisfactory. The best results have been obtained with glasses of high melting point and low alkali content, that is to say, by regarding the hardness as related to the composition of the glass, rather than by endeavouring to treat ordinary glass so as to increase its hardness by physical means. An early method of hardening glass was to plunge the hot material in oil, but a bath of molten lead and tin sometimes gave superior results. Quenching with jets of steam or cold air is now used.

Hardened glass is practically unbreakable, but if it is scratched it may suddenly fall to powder. This is an advantage in motor car windows, etc., as it reduces the risk of serious injury to the occupants in case of accident.

The **bending** of glass is effected by heating it sufficiently to make it soft. Glass tubes may be heated in an ordinary batswing gas flame, rotating them carefully so as to secure uniform heating, and then bending them to the desired shape. Sheets of glass are bent by placing them on a bed of whiting or of iron covered with asbestos, and placing them in an oven hot enough to cause the glass to bend to the shape of the bed on which it is placed. Small pieces of glass are usually bent by the makers by holding them in the mouth of the furnace until the glass is sufficiently soft, and then bending it as desired. The secret of satisfactory bending consists in getting the glass of the right softness; it must not be overheated or it will lose its shape, nor irregularly heated or it will give a poor result. Curved car lights may be bent to shape by pressing the heated sheets between wooden templates.

The **cutting** of glass is usually effected by the glass-blower allowing a few drops of water to fall on the hot glass, or by touching it with a cold piece of iron. For cold glass a diamond may be used, or one of the hardened steel wheels now largely used as substitutes for glaziers' diamonds. It is sometimes convenient to make a scratch on the glass with a file, and then to bend it sharply until it breaks, or to draw an imaginary line from the scratch in the required direction, by means of an exceedingly small flame. The flame cracks the glass in its immediate vicinity, and with care the crack can be made to extend in any direction. Small sheets of glass can also be cut by immersing them in a bowl or tank of water and cutting them with scissors. It is necessary that the scissors and hands of the workman shall be fully immersed.

Technically, the term "cutting" relates primarily to the production of lines on the surface of the glass, these being made by means of a rapidly revolving steel disc or **wheel,** the edge of which performs the operation, being aided therein by sand or other abrasive. For the final polishing a wooden or cloth wheel and putty powder or whiting are used. For smoothing or grinding, wheels made of sandstone or emery are used, the glass and wheel being both kept wet during the operation. In some works a stone or corundum wheel is used for cutting, and some manufacturers prefer to finish the ware by dipping it in a mixture of hydrofluoric and sulphuric acids which leaves a polished surface.

Ground glass is made by rubbing the surface with sand or other abrasive and water, but acid sodium fluoride is also used as a corrosive, which acts more rapidly and uniformly than any abrasive. Sand-blasting is also used (see "Frosting").

Engraving is similar to cutting, but no abrasive is used, the work being usually done by copper discs revolving in a small lathe. Some engraved glass is extremely costly, and demands the exercise of the highest skill. **Cameos** are made by uniting two pieces of glass together, the white one forming the front is then cut away where it is not required, leaving a white relief design on a background of a different colour. Quite recently, the demand for very cheap cameos has resulted in the production of moulded designs which are fastened to background pieces with cement. Such a method lacks the accuracy and cannot produce the sharpness and delicacy of cameos cut directly from the glass, and is only useful for interior work.

Etching and **embossing** are usually effected by means of hydrofluoric acid, which corrodes and dissolves glass exposed to its action. The glass must, therefore, be protected by a covering of wax or other insoluble material in those parts of the design which are not to be etched away. If "flashed glass"—*i.e.*, glass which has a film of glass of a different colour on its surface—is treated in this manner, the design can be in matt or transparent glass on a coloured ground or vice versa. A matt surface may also be produced by painting the appropriate parts of the glass with a mixture of hydrofluoric acid and ammonium chloride.

Frosting is usually effected by sand-blasting the glass so as to roughen the surface, then covering it with strong glue and leaving it in a warm room. As the glue shrinks it tears away sufficient of the glass to leave a frosted surface (see also "Ground Glass").

The use of the **sand-blast** in glass working is very extensive, as it is rapid, cheap, and capable of application in a number of different ways. The process consists essentially in blowing a fine spray of sharp sand on to the surface of the glass, any portions requiring to be left polished being covered with a stencil through which the sand cannot penetrate. The minute angles on the grains of sand cut away fragments of the glass, leaving a surface which is remarkably uniformly roughened if the operation has been properly carried out.

Iridescent glass is made by producing tiny flakes on the surface of the glass, these flakes refracting and reflecting the light in such a manner as to produce the phenomena of iridescence. In antique glasses the iridescence is usually due to the prolonged burial, allowing time for the moisture in contact with the glass to have produced the necessary flaking as a result of corrosion. Iridescent glass is usually made by exposing the ware to the action of a 15 per cent. solution of hydrochloric acid under pressure, or by sprinkling stannous chloride on the edge of the furnace, and allowing the fumes to act on the glass.

Light Bulbs.—Fifty-six men can produce about 40,000 light bulbs per 8-hour shift by traditional hand-blowing methods. This operation, too, is now done on automatic machines. The Westlake or Kadon machine, a further development of the Owens, simulates the operations of the hand-blower and a single 12-arm machine is capable of producing about 40,000 bulbs in 24 hours. A later machine of a similar type, the Ivanhoe, takes up only half the space but is capable of producing twice the number of bulbs per 24 hours. This has since been surpassed by a ribbon-type machine which works on an entirely different principle and is capable of producing the phenomenal number of 400 bulbs per minute with a single human operator. In contrast to the other machines, the glass is fed continuously from the tank through two rollers which press it into a band or ribbon with a series of circular bosses on one side. These bosses register with holes in the supporting conveyor and later with a series of travelling blow-heads, which first blow the glass into a series of hollow parisons and subsequently, after registering with rotating, paste-lined moulds, into light bulbs. The bulbs are produced so quickly that only a selected few are critically examined at intervals instead of the whole production. One such machine working twenty-four hours per day can replace 540 shops of hand-blowers working an 8-hour shift.

Frosting of Light Bulbs.—Light bulbs are frosted by inverting them in racks and spraying the inside with a solution of $H_2F_2-NH_4HF_2$ followed by H_2F_2 alone. After each acid treatment, water sprays remove the acid and reaction products. Finally the bulbs are dried in a current of warm air.

Finishing Hollow-ware.—Automatically made press- and blow-glass ware, if it is to be in the form of pieces open at the top, such as tumblers or drinking glasses, must undergo a finishing operation. The unwanted glass is cracked off or melted off by intensely hot flames impinging at the correct height on the rotating article. The edges are smoothed or "glazed" by passing through a softer gas flame, if necessary after a preliminary grinding square followed by thorough washing and drying. They should finally be passed through an annealing lehr to remove strains.

Pressed Ware.—While in the viscous plastic state, glass can be pressed to fill a form or mould, much in the same way as plastic clay in the pottery industry. By pressing in carved moulds a very good imitation of cut crystal can be obtained. The process is not, in general, fully automatic and, particularly with complicated forms, a certain amount of teamwork and manual dexterity is required.

By means of a gob feeder a charge of glass of predetermined size, shape and weight can be delivered into the mould at the desired temperature. The cheapest types of ware receive no further treatment and after cooling are ready for sale. Better class wares are fire-polished before going on to the annealing lehr. In the course of this operation any further changes of form required may be imposed; likewise sticking up operations may be carried out. The fire polishing removes slight roughnesses and gives the article a brilliant surface appearance.

A semi- or fully automatic press with 8 moulds can produce up to 1,200 articles of simple form, *e.g.*, drinking glasses, per hour.

OPTICAL GLASS

The production and working of optical glass differs in many respects from those previously described. Owing to the peculiar requirements of the makers of modern scientific instruments, far more attention has to be paid to the minor characteristics of optical glasses and, consequently, they are much more expensive than other forms of glass. Moreover, at least 60 per cent. of the glass made for optical purposes must be discarded on account of small defects, so that the amount of material made is out of all proportion to that actually entering into the finished instruments.

Defects which would have been overlooked a few years ago are now regarded as of sufficient importance to disqualify glasses for some instruments, and the enormous amount of research carried out by the leading firms of optical glass manufacturers has resulted in the production of glasses of a quality and power quite undreamed of a few years ago. The two chief difficulties with which the manufacturer of optical glass has to contend are the production of a "metal" of complete uniformity and freedom from specks, striæ, tensional and other strains and the possession by the glass so produced of the requisite optical characteristics to enable it to be used in the instrument for which it is made.

The composition of most optical glasses resembles that of crown and flint glass, respectively, pieces of each of these glasses being used in combination in order to produce the requisite refraction of the light, and to form an image free from distortion and rings of colour (*i.e.*, **anastigmatic** and **achromatic**).

Light from the blue end of the spectrum, when passing through flint glass, is dispersed more than that passing through crown glass, so that the older combinations were not entirely free from chromatism. The most recently made glasses of the best-known firms are, however, so adjusted by varying the composition of the glasses forming the combination of prisms or lenses as to reduce both dispersion and chromatism to the minimum. Thus the blue end of the spectrum is shortened by replacing some of the silica by boric acid. The use of baryta, magnesia, alumina, and zinc oxide also affects the optical properties of glasses. Lanthanum, thorium, etc., are also used in optical glasses.

The chief **optical constants** which determine the use of a particular glass are:—

(*a*) The refractive index for the sodium line (D) in the spectrum, $= \mu_D$.

(*b*) The mean dispersion for lines C to F in the spectrum, $= \Delta$.

(*c*) The ratio of refractive index to mean dispersion, $\nu = \frac{\mu_D - 1}{\Delta}$.

The refractive index is closely related to the specific gravity of a glass, and is varied by any changes in the latter. The dispersion varies with the composition of the glass, being lowest with glasses rich in boric and phosphoric acids, and highest in glasses rich in bases. Hence flint (lead) glasses are largely used on account of their high refraction and dispersion, but low ratio. If low dispersion and refraction are required, crown (alkali-lime) glasses are used, though they have a high ratio. Baryta glasses have a high refraction, a low dispersion, and a high value for ν. Unfortunately, the optical properties of glasses and combinations are limited by the chemical stability of some of the glasses which can be produced. Thus boric and phosphoric glasses may only contain a small proportion of alkali; otherwise they are hygroscopic and soon become opaque. Some other possible compositions are useless because of their rapid devitrification.

Other qualities desired in optical glasses are:—

Transparency and freedom from colour: though the presence of small bubbles and of a decidedly greenish-yellow colour do not interfere with the use of some glasses as lenses, and technical perfection in the glass is often sacrificed to other optical properties and to cheapness.

Homogeneity or freedom from **striæ** and other irregularities. It is important to test for these by examining the glass in a beam of truly parallel light, when the striæ appear as alternating bands or lines. For many purposes inclusions and bubbles are less serious than striæ (see "Defects," p. 285).

Hardness, so that the articles made from the glass will not be unduly spoiled by the ordinary processes of cleaning.

Chemical stability, in order that the glass may not devitrify or become opaque.

Absence of internal strain, so that there may be no undue distortion or tendency to fly to pieces. This is secured by careful annealing.

Suitable **refraction** and **dispersion.** The refractive index of most glasses lies between 1.4 and 1.9, as outside these limits the glasses are unstable. Several transparent minerals, such as fluorite, have much larger refractive indices. Lanthanum, thorium, and barium favour high refraction and low dispersion.

The **manufacture** of optical glass consists in melting the ingredients which it is expected will produce a glass of the desired characteristics, a crucible with a cover (Fig. 2) being used for the purpose. The molten mass is freed from gall or scum from time to time, and is heated intensely so as to clarify it (p. 277). When test pieces indicate that the glass is satisfactorily clarified, the stirring is begun (p. 277), and is continued until the glass is almost solid, a fire-clay cylinder or a porcelain rod being used for this purpose. Usually the glass is then allowed to cool slowly, and when quite cold the pot in which it was melted is broken up and the best pieces of glass are selected for use or for remelting.

At the Jena works a more elaborate process of cooling is used, the glass being maintained at a temperature of 470°–570° C. for several weeks, and if the glass is required for very special work, such as large lenses, it is remelted and recooled several times, as many as ten such treatments not being unusual. Thus for the objective (36-in. diam.) in the Lick telescope, no less than twenty castings were necessary, and its manufacture occupied four years.

The difficulty of preparation and the enormous amount of experimental work required, particularly in the endeavour to make improvements in the glasses manufactured, make optical glasses of the best qualities exceedingly costly, and it is doubtful if they can be made on a large scale at a profit until melting pots of a much greater refractoriness and resistance to corrosion have been invented. These would enable much higher temperatures to be reached, and would greatly facilitate the manufacture of the glass. At present, electrical furnaces appear to be unsuitable, but platinum crucibles have justified themselves in use despite the high initial cost.

SPECIAL GLASSES

With the development of science, and its increasing application to practical and industrial matters, has arisen a demand for a number of different kinds of glass, each having one or more special properties in addition to those for which glass is generally known. These special glasses are conveniently considered separately.

For **chemical purposes** glasses are required which have a high degree of resistance to chemicals and to sudden changes in temperature.

Such glass is now manufactured by several firms, but was first made on a commercial scale in the famous works of **Schott & Abbe** in Jena, and sold under the term **Geräte glass**; its definite composition has never been published by the manufacturers, and some analyses which presume to give this information are by no means correct. It is, however, admitted to be a baryta glass containing boric acid and alumina, with little or no alkali. For English substitutes see p. 276.

For **steam boiler gauges** and similar purposes the Schott **Verbundglas** is specially useful, and has a resistance to chemical reagents which is five or six times as great as that of ordinary glass. This glass is sold under the name **Durax,** and is a boro-silicate glass. **Pyrex,** a British heat-resisting glass, contains 80 per cent. SiO_2, 12 per cent. B_2O_3, 3 per cent. Al_2O_3, and 4 per cent. Na_2O.

For lamp and gas burner **chimneys** a glass of exceptional thermal endurance is required, as the heat from an incandescent mantle is exceedingly great.

The Jena works have therefore placed on the market chimney glasses made of a boro-silicate which is very infusible, and yet not sensitive to sudden cooling. This glass is reputed to have a composition corresponding to 66 per cent. silica, 24 per cent. boric acid, 4 per cent. antimonious acid, and 6 per cent. soda. For an English substitute see p. 276.

Glasses which are **transparent to selected rays** are important in some surgical and other work. Thus, the ultra-violet rays are damaging to some eyes, but protection may be obtained by using glass such as that invented by Sir Wm. Crookes, which is impervious to the rays it is desired to avoid.

For use in mercury vapour lamps and other purposes, where it is desired to utilise the powerfully actinic ultra-violet rays, a glass invented by Zschimmer, and made at the Jena works under the term **Uviol glass,** is valuable. This glass is based on Zschimmer's discovery that the ultra-violet rays are stopped by metallic oxides in the glass, lead being the strongest, soda next, and potash the weakest in this respect as regards a boro-silicate glass. Sackur, on the contrary, has produced a glass which is opaque to all the photographically actinic rays by heating the glass with a mixture of sulphide and sulphate of silver. The silver is reduced to the metallic state and colours the glass brown. **Corex,** a calcium phosphate glass, has high ultra-violet transmission.

Glass substantially opaque to visible light but with a high transparency to infra-red was developed during the 1939-45 war for special purposes. A lead glass high in manganese has such properties.

For **electrical insulation,** a boro-silicate glass containing baryta and lime, but free from alkali, has been found by Schott to be highly satisfactory.

For **thermometers,** a whole series of special glasses are now made, according to the particular purposes for which the instruments are to be used.

Most glasses expand slightly on repeated use as thermometers, so that the instruments give a lower reading than they should do. This phenomenon is known as depression. It is most marked in glasses containing both potash and soda; glasses which contain only one of these oxides are better, but two of the glasses made at the Jena works are quite free from this defect. Glass 16 III. consists of 67.3 per cent. silica, 2 per cent. boric acid, 14 per cent. soda, 7 per cent. lime, 7 per cent. zinc oxide, 0.2 per cent. MnO, and 2.5 per cent. alumina. No. 59 III. consists of 72 per cent. silica, 12 per cent. boric acid, 11 per cent. soda and 5 per cent. alumina: it is very refractory, and is largely used for nitrogen thermometers for measuring temperatures up to 500° C. No. 16 III. is used all over Germany for the manufacture of thermometers and hydrometers. Moreover, it is easily worked in the blow-pipe on account of its content of boric acid and alumina.

Artificial gems are made of **strass** or **paste,** which is a dense lead (flint) glass with the highest available refractivity, and may be regarded as a special kind of optical glass. Most natural stones are crystalline, and cannot therefore be perfectly imitated by any amorphous glass. By cutting the glass so that it may have similar facets to the genuine stones, however, sufficiently good imitations may be made, though glass can never be as durable as true stones. The raw materials used must be specially purified, so as to obtain the greatest possible transparency, clearness, and freedom from colour, particularly for imitation diamonds. A typical mixture consists of powdered quartz 100 parts, red lead 157 parts, caustic potash 54 parts, boric acid 5 parts, and white arsenic ½ part.

The compositions of a number of special glasses are given below (after Butterworth).

CHEMICAL COMPOSITIONS OF SOME SPECIAL PURPOSE GLASSES (A. Butterworth).

	"Vycor."	"Pyrex."	H.P. Hg Vapour Lamp.	Na Vapour Lamp.	"Corex" high U.V. Trans.	Dense Flint Optical.	Lindemann X-ray Trans.	X-ray Prot.	Iron Seal.	Shut.
SiO_2	96.3	80.07	8.7	21.5	2.12	20.0	...	28.0	45	72.29
B_2O_3	2.9	12.0	3.0	40.0	4.63	...	82.1	...	...	...
TiO_2	...	0.05	0.04	...	...	...	...	...	...	...
Al_2O_3	0.4	3.0	22.4	22.0	0.37	...	...	...	...	1.66
Fe_2O_3	0.4	0.08	0.12	...	0.03	...	...	...	...	1.66
CaO	0.2?	0.20	5.9	10.0	25.10	...	...	...	...	8.77
MgO	...	...	8.4	...	0.60	...	...	...	...	2.99
BaO	...	...	...	...	...	...	...	10.0	...	...
PbO	...	...	...	...	...	79.9	...	62.0	30	...
Na_2O	0.02	3.9	1.1	6.5	0.56	...	...	...	6	12.96
K_2O	0.02	0.32	0.2	...	...	...	...	...	14	0.87
As_2O_5	0.005	0.30	...	...	...	0.1	...	...	...	...
P_2O_5	...	...	...	...	66.45	...	...	...	...	...
Id_2O	...	...	...	...	...	...	15.3	...	...	...
BoO	...	...	...	...	...	...	2.6	...	...	...
CaF_2	...	...	...	...	...	...	...	...	...	0.23
SO_3	...	...	...	...	...	...	...	...	...	...

DEFECTS IN GLASSES

The chief characteristic of ordinary glassware is its transparency, freedom from colour and lustre. In the best modern glasses these properties are retained without difficulty under ordinary conditions, but the ancient glasses—which were necessarily rich in alkali in order to be of the requisite fusibility—suffer from a species of corrosion which is commonly termed **decay.** This is specially noticeable in the antique glasses preserved in museums and elsewhere.

The defects of glasses may be arranged in three groups, as suggested by Pazaureck:—

(*a*) Glasses which have been badly manipulated by the workmen engaged in their manufacture. Such glasses contain bubbles, inclusions of unmelted particles, particles of reduced lead, caused by stirring a flint glass with a wooden stick, striæ, and other signs of lack of homogeneity. Nothing can be done with such glasses when they have once been made into articles (see p. 283).

(*b*) Glasses which have decayed by exposure to unsuitable conditions. The most frequent cause of trouble in this respect is the too vigorous cleaning of the glass with strong detergents, such as caustic alkalis or mixtures of soap and fine sand. Some glasses will be corroded if left wet for a long time, as the water has a perceptible action upon them. As the interior of the glass is usually softer than the outside, owing to differences in the annealing, extensive abrasion of the outer film only increases the tendency to decay. Glasses should, therefore, be well rinsed in clean, soft water after washing, wiped quite dry, and, if valuable, stored in dry and dust-proof cabinets.

(*c*) Glasses of defective composition, this being the cause of their decay. Such glasses will devitrify in course of time, or will develop colours which they did not originally possess. The development of a colour after exposure to intense sunlight, or to some of the more actinic rays produced in electric lamps, is often due to the use of insufficient decolorant (p. 273), but this is by no means invariably the case. The colour may sometimes be discharged by heating the glass to dull redness. The precise cause of this coloration has not been fully explained; it is not improbably due to some rearrangement of the electron shells of atoms within the glass network, brought about by the action of light or other radiant energy. Some suggestions with respect to this will be found in the section on the "Constitution of Coloured Glasses" (p. 294).

Mattness or turbidity is sometimes due to the production of minute hair cracks on the surface of the ware; this may be followed by spalling or flaking.

Cut glass tends to decay more rapidly than plain or moulded, as the cutting removes a portion of the harder external film and exposes the softer glass beneath. There is no remedy for this, as an effective reheating and annealing would destroy the beauty of the article by rounding the sharp edges of the design.

The decay of glass is not due to a contagious disease, as is often supposed by the ignorant, but to the fact that all glasses are slowly soluble in water, those which are rich in alkali being the most readily attacked.

OPAQUE AND COLOURED GLASSES

The production of coloured glasses forms an important branch of the industry of glass-making, though most of the colours employed have been in use for many years, and some of them for several centuries.

The improvements which have made possible some of the most beautiful of modern coloured glasswares are, therefore, due to the use of pure colours, and of improvements in the manufacture of the glass itself, rather than to any striking discoveries in the form of new materials. An exception to this general statement may, perhaps, be found in the case of the selenium compounds, which will be mentioned later.

The question, "What makes certain glasses coloured?" is extremely difficult to answer. It is not sufficient to state that the colour is due to certain coloured silicates, unless the precise compounds are stated, and this is usually omitted, or expressed in very indefinite language by writers on this subject. The reason is simple, and is due to the general conception of glasses as mixtures of various substances in a semi-fluid state, *i.e.*, in the state known as a "solid solution" (p. 262).

If, on the contrary, glasses are recognised as being definite chemical compounds (though like most commercial compounds they are not in a pure state), much of the difficulty of understanding their constitution is avoided; this is especially the case with coloured glasses. The difficulty of proving in a simple manner that glasses are really definite chemical compounds is, however, very great, as glasses do not all belong to one class of compounds, some being much more complex than others in their composition and attempts to do so have now been virtually abandoned.

According to W. & D. Asch, most, if not all, glasses are composed of a series of ring compounds (p. 255), and at some of the points of combination various metallic oxides may be introduced into the molecule. These positions are marked with a + in the formulæ on pp. 255–256. It is these metallic oxides in combination with the immediate silica groups which were considered to form the chromophore or colouring agent.

Aventurine glass contains a little free copper, distributed irregularly in the form of fine lamellæ. Some investigators attribute the characteristic appearance of this glass to these lamellæ. The presence of free copper was proved by Wöhler who extracted the metal with mercuric chloride, and by Zulkowski who converted it into cuprous oxide by means of an ammoniacal solution of copper sulphate. Zulkowski has also proved that porpora and copper ruby glass contain no free copper when properly made. His researches also destroy the foundation for the view that the colour of these last two glasses is due to the glass holding metallic copper in solution. Bontemps and, somewhat later, Seger found that many different colours can be produced from the same mixture by altering the conditions of firing, and particularly of the nature of the gases entering the crucible or glass-pot. This may be explained by regarding the atoms immediately connected with the copper in the compound as forming a chromophore group; if the glass is exposed to reducing conditions the oxygen is removed from this chromophore group and the glass is converted into a dark grey or black mass, but on treatment with an oxidant the red colour is restored.

It has long been puzzling to understand why so small a proportion of colouring agent could affect so large a proportion of glass. This fact is, however, a direct consequence of Asch's theory and formulæ, and a further consequence is that the maximum possible content of colouring oxide is definite and necessarily small; its amount for any metal is determined by the number of molecules which can be introduced into the formula at the points able to take them. If analysis shows more copper (or other metal) than can be accommodated at these points, the remainder must exist in the free state (as in aventurine glass).

Whilst the application of this theory of the constitution of coloured glasses has not yet been applied individually to many of the products of English glass-works, the success met with on its application to glasses of German and French origin merits its further study in this country. It is not, of course, necessary that a coloured glass should consist exclusively of one kind of compound; on the contrary there is evidence that some coloured glasses consist of a coloured glass mixed with a colourless one. Seger's ruby glass made by adding 1 per cent. of copper to a glass corresponding to $6Na_2O.6CaO.6B_2O_3.30SiO_2$ appears to be of this kind, as the chromophore group can retain 4 per cent. of copper in the molecule.

Fortunately, the manufacture of coloured glasses has reached a high degree of perfection quite apart from any accurate knowledge of the chemical constitution of the glasses, for the colours can, in most instances, be formed by adding a suitable oxide to the glass mixture and then submitting the contents of the pot or crucible to such oxidising or reducing flames as experience has shown to be necessary. Two methods of colouring are used: the colouring agent is mixed with the whole bulk of the glass which is then known as **pot-metal colouring,** or a little coloured glass may be applied to the surface of the glassy mass, this being known as **flashing.** Flashing is obviously far cheaper in some instances than is pot-metal colouring, but with cheap colouring agents, such as iron, there is little difference in the two methods.

A third method of colouring glass consists in painting pieces of colourless sheet glass with more fusible glass to which suitable colouring agents have been added; this method is used for the **stained glass** employed for windows in churches, etc. After painting, the glass slips are reheated in a small muffle furnace so as to fuse the coloured glass without affecting the background on which it is painted.

The following colours are produced with the oxides named below:—

Green glass is usually produced by iron compounds, which form a variety of shades according to the form in which the iron is introduced. Magnetic oxide or a mixture of ferrous and ferric oxides produce the typical "bottle glass green"; purer ferrous oxide produces a bluish green; ferric oxide produces a yellow or yellowish green, the yellow tone being strongest in flint glasses. Under some conditions—possibly with reduction of the iron to the metallic state—a purple-red colour is formed.

Chromium oxide also produces green glasses, but they are more or less yellow if the conditions in the furnace are unfavourable. It is usually added in the form of potassium bichromate, and care must be taken not to add excess or it will render the glass turbid without giving it the desired colour. The so-called **chrome aventurine** is made by using an excess of chrome, which crystallises out in the form of minute green crystals, reputed to consist of chromic oxide. Copper oxide also produces beautiful green glasses, providing it is fully oxidised. Mixtures of chrome and copper were used for the green wine glasses of the Romans.

Blue glass is sometimes made by adding copper oxide to a glass rich in silica and alkali, when a rich sky blue may be obtained, but the chief agent for the production of blue glass is cobalt oxide. So powerful is cobalt that 0.1 per cent. of it will produce a deep blue glass. The colour is changed to violet in the case of soda glass, and to sky blue in the presence of a little iron or copper.

Violet glass is usually made with manganese compounds, the composition of the glass affecting the colour; thus soda glasses are reddish violet, potash glasses are bluish violet, and so on. The colouring power of manganese is somewhat weak, and upwards of 6 per cent. is generally necessary. Manganese compounds are very sensitive to reducing agents, and their colour is generally discharged if the glass melt containing them is subjected to reducing gases. They are, therefore, a valuable means of decolorising some glasses. Nickel oxide produces violet glasses, but is somewhat uncertain; the best results appear to be obtained with potash-lead (flint) glass.

Brown glass may be produced by nickel in a crown glass, or by a mixture of manganese and iron oxide in other types of glass.

Yellow glass is commonly produced by means of iron compounds in the presence of an oxidant, such as manganese, by the addition of an excess of red lead, or by the use of uranium oxide. Finely divided carbon (charcoal) also makes glass yellow, especially in the presence of sodium sulphide. Sulphur compounds are valuable colorants, and the yellow glasses they produce are specially useful inasmuch as they are selective in action, and do not permit ultra-violet rays to pass through them. For this reason, they are valuable in glasses used for storing liquids which are sensitive to light, such as beer, solutions of silver salts, etc. Lead antimoniate is sometimes used for glasses with a yellow opacity.

Black glass, like black porcelain, is unknown; the nearest approach to it is a very dark violet or blue with some brown in it. Such a glass may be made by mixing cobalt, manganese, and iron oxides with the glass. A dark hyalite glass is also made by adding ferric sulphide to bottle glass; the sulphur and iron combine to produce a glass which, for many purposes, is sufficiently dark to be regarded as black.

In borax glasses, copper oxide and manganese dioxide give better results than manganese dioxide and cobalt.

Pinkish shades are frequently made by flashing with a thin film of red glass, but pot metal can be coloured pink with tellurium, or with selenium compounds.

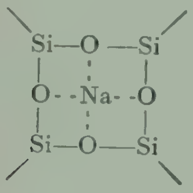
Red glass may be made with either gold or copper as the colouring agent. An extremely small proportion of gold is necessary, and it is commonly understood to be in the form of a colloid or suspension of the metal, the particles of which are so fine as to be distinguished only by the ultra-microscope. Zsigmondy estimates their diameter at 0.00001 mm. One of the best methods of preparing gold ruby glass is to precipitate the gold with colloidal stannic acid, and to add this to the glass. A yellowish glass is usually formed at first, but on reheating it turns to ruby; the heating must then be stopped, as prolonged or excessive heating spoils the colour. Copper red glasses are of several kinds; three important ones being *porpora*, *copper ruby*, and *aventurine*. The best results are obtained with a flint glass to which a small proportion of cuprous oxide, a little stannic oxide, and a reducing agent are added. The glass produced is almost colourless, but its colour is developed by reheating in a muffle.

Silver stain is a term applied to the yellow colour produced on glass which has been painted with a mixture of clay and silver nitrate and then heated in a muffle. The silver penetrates the surface of the glass and produces a permanent yellowish stain. This method is extensively used in the production of yellow signs on a transparent ground.

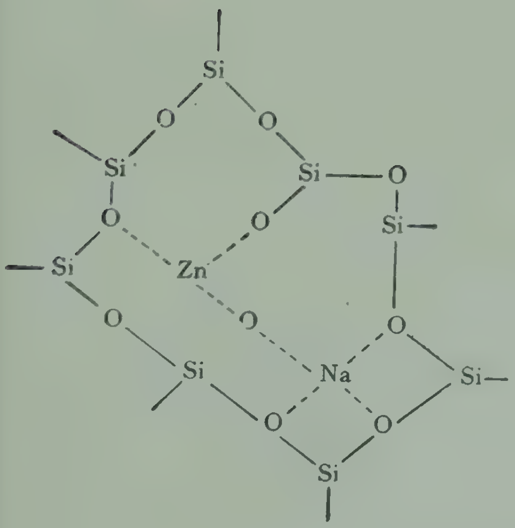
White opaque glass is made by adding an insoluble white oxide to the glass. There are several substances available for this purpose, the chief of which are cryolite, felspar, fluorspar, calcium phosphate (bone ash), tin oxide or even silica. The best opacifying media are those which dissolve completely in the molten glass but devitrify or crystallise out on cooling. The crystals must be extremely minute, and in many cases they are so small as to render it doubtful whether the opaque material is not amorphous. Tin oxide is an exception to the rule just stated, as it is an excellent opacifier, but does not dissolve in the molten glass to form a clear solution. The oxides of antimony and arsenic are also used as opacifiers. **Opal** and **alabaster glass** have a smaller proportion of opacifying agent than the more opaque glasses, but otherwise they are of the same nature. **Milk glass,** such as is used for the backs of thermometers, on the contrary, may contain as much as 30 per cent. of the opacifying agent.

Gilded glass is an important feature of many articles imported from Bohemia. The gilding is effected by the use of a solution of gold in a special balsam, the mixture being sold by dealers in glass-makers' materials under the term "Liquid Gold." This solution is applied to the parts to be decorated, and they are then heated in a muffle furnace to a dark red heat. This produces a bright gilt which requires no burnishing. The same process is used in pottery manufacture.

Modern Views on Constitution of Glass.—Although modern ideas regarding the constitution of glass have moved away from the more rigid formulations of the Asch brothers and others, there is still a formal resemblance, *e.g.*, in views as to the mode of attachment of the glass modifiers. These may be regarded as modifying or breaking the oxygen-silicon linkages at various points in the network. In the case of a "weak" cation, there may be no actual breaking of Si—O bonds but the cation will be accommodated by coordinate links and there will be some polarization, *i.e.*, distortion of the Si—O bonds. Thus sodium may be considered as surrounding itself with six oxygens (only four of which are shown in the two-dimensional representation): —

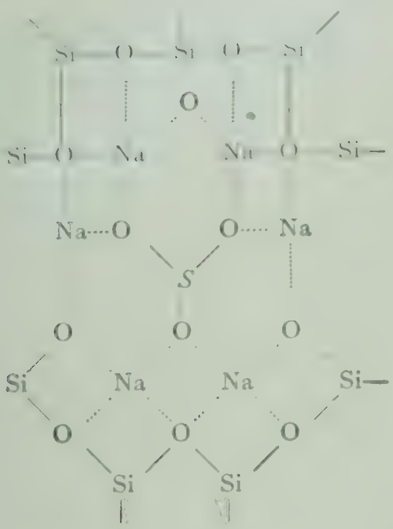


(*a*) weak cation: all-sided coordination linkage to (SiO_4) network.



(*b*) medium strength cation: partial linkage through weaker cation.

(After Dietzel)

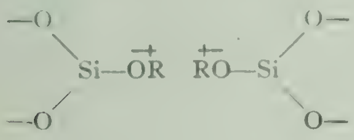


(*c*) strong cation (*S*): linkage to network only via weak cations; tendency to unmix.

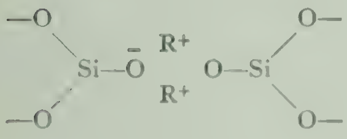
(After Dietzel)

In the case of a medium strength cation such as zinc the coordination linkage will be partly to an oxygen linked to silicon and partly to a weaker cation, the presence of which is necessary to prevent demixing.

Other authors postulate a more or less complete rupture of the (SiO_4) network at points where cations are accommodated thus:—



(*a*) cation with strong field: strong loosening effect.



(*b*) cation with weak field: weak loosening effect.

(After Endell and Hellbrügge)

Some of these schemes may appear to be almost as fanciful as the formulæ of the Asch brothers, but it must not be forgotten that the subject is one of considerable difficulty and our ideas with regard to the structure of glass are still in course of being formed.

The behaviour of coloured ions in glasses, more specifically those capable of producing more than one colour, is explained by analogy to their behaviour in crystals. Thus in the case of copper, the group (CuO_6), *i.e.*, the copper atom in 6-fold coordination with oxygen, is blue. Two of these oxygens are more easily polarised than the other four and the expanded form is green. Copper in four-fold coordination with oxygen (CuO_4) is yellow-brown. Normal alkali-silicate glasses are coloured blue by copper oxide. The (SiO_4) network is sufficiently modified by the alkali ions for the copper atom to be able to achieve practically complete coordination. If some of the alkali is replaced by boric oxide, the coordination possibilities for copper are diminished and the colour changes. The coordination possibilities for Cu may be diminished to such an extent that colloidal CuO (or Cu is precipitated in the glass.

The fully coordinated lead ion is colourless. If the lead content of a glass is increased considerably at the expense of alkali, the lead ions may not be able to achieve their full coordination of 8 or 12 oxygen atoms and the yellow colour of PbO makes itself apparent. The yellow colour of cadmium-rich glasses can probably be explained in a similar manner.

In iron-containing glasses a pure yellow colour probably indicates iron in six-fold coordination, whereas a green colour probably indicates that the coordination is four-fold.

Uses of Coloured Glasses.—The greater part of the coloured glass made is used in the form of fancy articles, though large quantities are also used in the form of sheet for windows and decorative work. Thin sheets of opaque white glass, cut to the size of bricks, are also largely used as a substitute for glazed bricks for the lining of operating theatres and other buildings where sanitation and cleanliness are of first importance. In many instances it would be better to use much larger sheets, and the success attained by these in a few instances is likely to lead to their extended use.

Articles for table or decorative purposes may have designs worked on or in them by means of coloured glass, applied by the maker during the process of blowing and working. Thus a small piece of opaque or coloured glass may be attached to a wine-glass in course of formation, and by twisting the coloured glass in various ways many intricate and pleasing designs may be produced in a simple manner. Some of the work done in this way by the ancient Venetians has never been surpassed either in the skill of the workmanship or in the taste displayed in the design used. The tendency at the present day is, however, to avoid these delicate designs and to apply the colour in larger and simpler masses. Lithographic transfers are also used as in pottery decoration.

A comparatively new use for coloured glass is in the production of tiles for walls or floors. These are known by various fancy names, Garchy's **Keramo** being one of the earliest of these terms. The material is made by heating broken glass until it devitrifies, and then more rapidly until it fuses sufficiently to bind the crystals together. The felt-like arrangement of the crystals produces a material as strong or stronger than tiles made of earthenware and of equally good appearance. By cutting the blocks of devitrified glass into irregular blocks and arranging them as a terrazzo or mosaic, an extremely handsome effect may be produced. The blocks may then be united by means of a mortar of powdered fusible glass, the whole being heated until this glass fuses, or Portland cement mortar may be used.

REFERENCES

(1) Alexander Silverman, *Ceramic Bulletin*, **26**, 367 (1947).
(2) A. Dietzel, *Naturwissenschaften*, **29**, 81 (1941); **36**/37, 537 (1941).
(3) J. E. Stanworth, *Trans. Soc. Gl. Tech.*, **30**, 54 (1946); **32**, 154 (1948).
(4) F. Singer, "Glass Industry" (1950).

QUARTZ GLASS OR FUSED SILICA GLASS

LITERATURE

J. BRONN'S "Elektrische Ofen in Dienste der keramischen Gewerbe und der Glas- und Quarzglaser-zeugung." Halle, 1910.
J. F. BOTTOMLEY.—"Seventh Intl. Congress Applied Chemistry," II., 181.
C. COLNE.—"Metallurgical and Chemical Engineering," IX., 226.
ANON.—*Chemical Trade Journal*, XLVI., 61, LII., 104.

Modern facilities for the production of exceedingly high temperatures permit the fusion of materials at one time considered quite infusible, and amongst other substances now obtainable in commercial quantities, as a result of the existence of these facilities, is quartz or sand which has been brought to a state of semi-fusion, and, on cooling, forms a substance with many of the properties of a glass.

There is a considerable diversity of opinion as to whether such a material should be termed a "glass," inasmuch as it is a single oxide, and not produced by the fusion of an acid (silica) with a base (soda, etc.). Those who term fused silica a glass refer to its physical properties alone, whilst those objecting to this term do so on the ground of its chemical composition. If, however, glasses are regarded as definite salts of the acid $H_xSi_yO_z$, it is clear that the fused silica must be regarded as the anhydride of the same type of acid, which may be closely related to the glasses, but is yet chemically distinct from them. At the present time, however, there is a strong tendency in some scientific circles to regard the term "glass" as conveniently applicable to a number of substances with approximately similar physical properties—the chief of which is that they are amorphous and highly viscous substances obtained by the relatively rapid cooling of a fused mass. Such a definition has its uses, but it tends to cause confusion with the slags—which are widely different from the glasses—and with a number of other substances of an entirely different composition and origin.

"Fused silica" consists essentially of almost pure silica; though often termed "quartz glass" this is incorrect, for the word "quartz" relates to one of the crystalline forms of silica, and on fusion it loses its distinguishing properties, and is therefore more desirably known by a term indicative of its composition. For this purpose, "fused silica" is convenient and suitable.

It is not correct to represent the composition of this fused silica by the symbol SiO_2, as it is in all probability a polymerised form of silica for which the symbol $(SiO_2)_x$ is more correct. It is not at present possible, however, to state the numerical value of x, nor the number of silicon atoms in a molecule of either quartz or fused silica.

The glassy nature of fused silica has been known for many years, but the use of an oxy-hydrogen flame for its production was considered to be too costly a process, so that it is only recently that its valuable properties have been recognised.

The earliest recorded production of articles from fused silica is that by Gaudin in 1839, and this was followed in 1869 by Gautier who prepared capillary tubes from this material. The first in this country to recognise the value of fused silica was Professor Boys, who, in 1889, prepared fine threads of the material for use in the measurement of minute forces. In 1901, Shenstone exhibited a number of articles of fused silica in a lecture before the members of the Royal Institution, and in the following year Heraeus quite independently prepared a number of other articles from the same materials.

Since that time enormous progress has been made, and the following firms have gained a world-wide reputation for their products:—

The Silica Syndicate Ltd., London, work in connection with an improvement of Shenstone's method, and produce a clear and transparent "glass."

W. C. Heraeus, G.m.b.H., Hanau, uses the method devised by Heraeus, and also produces a clear and transparent "glass."

Deutsche Quarzgesellschaft, m.b.H., formerly at Beuel on Rhine, used Voelker's method (p. 302), in which a cloudy "glass" was produced.

The Thermal Syndicate Ltd., Wallsend-on-Tyne, use J. F. Bottomley's process (p. 299), and also produce a semi-transparent "glass."

The Osram G.m.b.H., of Berlin, before and during the 1939–45 war used a process described in U.S. Patent No. 2,155,131, dated April 18, 1939.

Since their first inception, the methods of all these firms have been greatly improved, but for obvious reasons many of the improvements have been maintained as trade secrets, especially as regards the production of the largest pieces of ware. In any case, the production of such ware must be exceedingly difficult, as the temperature required varies from 1,700°–2,000° C. Briefly, the four firms mentioned work as follows:—

In **Shenstone's process** (now obsolete) the quartz is heated to 1,000° C. and is then thrown into water; it is then reduced to a very fine state of division without the particles falling to powder. The loose mass is next heated in an oxy-hydrogen flame until the particles melt one after the other and form a solid mass of "fused silica." This mass is wrapped round a platinum wire, and the coils are heated in the oxy-hydrogen flame until they fuse together and a tube is formed. This tube forms the basis of all further articles which may be made, as it can be melted together at one end, blown into flasks, etc., and generally worked like glass.

The **Heraeus firm** heats quartz for some time at 570° C., which causes it to break up into small pieces, which are afterwards fused in crucibles made of iridium. As this metal is costly and the crucibles are strongly attacked during the fusion, this method (like that of Shenstone's) is very costly. Quite recently this firm has patented the use of a mixture of zirconia and alumina for crucibles, and is using such a mixture at the present time. Carbon, lime, and clay crucibles cannot be used; the first reduces the silica to silicon, the second and last combine with the silica and form a slag-like material.

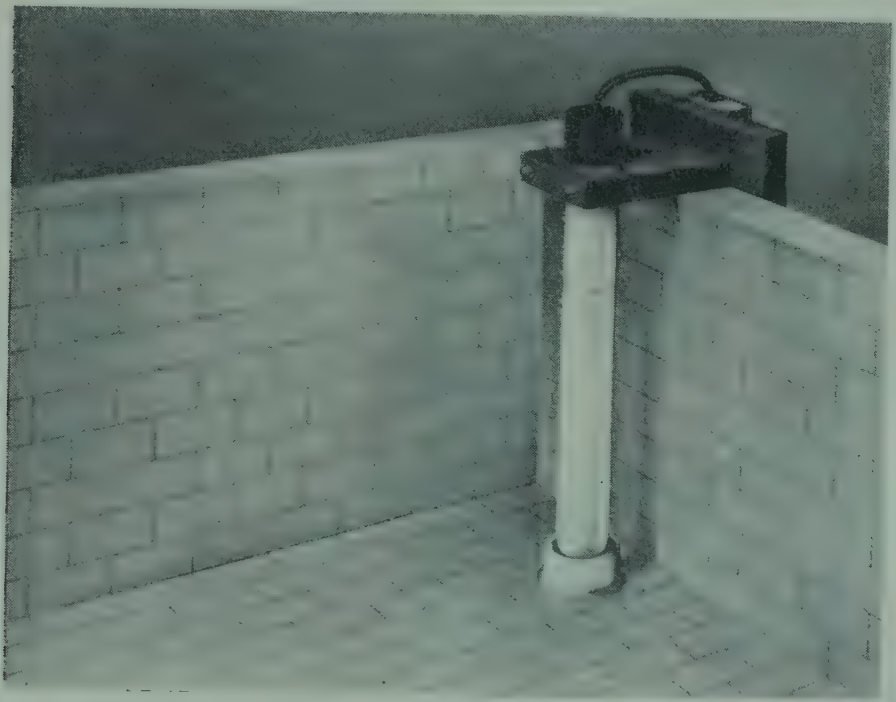


FIG. 19.—Vitreosil Electric Immersion Heater in Tiled Tank.
(*Courtesy, The Thermal Syndicate Ltd.*)

The fused material is worked like glass, and flasks of large capacity can be blown without any trouble. Means have also been found for casting the material in iridium moulds so as to obtain hollow cylinders, which are afterwards blown and worked in the oxy-hydrogen flame.

The **Quarzgesellschaft** and the **Thermal Syndicate** are able to work much more cheaply than those just mentioned, and the size of the articles they produce appears to be unlimited, coils of piping over 3 ft. high and basins 2 ft. in diameter having been shown by the latter firm at the International Congress of Applied Chemistry as long ago as 1910. The Thermal Syndicate use pure quartzose sand, which is heated electrically by means of a specially devised furnace, one electrode of which is embedded in the sand, whilst the sand itself forms its own crucible, as that which is furthest from the electrode remains unfused. The material is never completely fused, but is raised to a state of semi-fusion, so that the material possesses the requisite mobility for it to be worked like glass. Like glass which has been imperfectly cleared, it is cloudy and only semi-transparent. This ware is known by the trade name of translucent **Vitreosil,** and has a pretty pearly lustre in the smoothest parts.

Thermal Syndicate Limited can make pipes up to 30 in. bore and 4 ft. long in translucent Vitreosil. Longer pipes are also made, though with a reduced diameter. A good example of the industrial use of translucent Vitreosil is shown in Fig. 10, which is an immersion heater installed in a tiled tank. In addition to pipes and tubes, large pots and tanks are frequently made in the translucent material. Examples are round-bottom pots capable of holding 110 gallons of liquid, with overall height 5 ft. 4 in. and internal diameter 2 ft. 7½ in. Transparent Vitreosil, made from fused quartz, is generally used for smaller chemical and physical apparatus, though tubes up to 4 in. diameter and 6 ft. long can be made in this material. Examples of laboratory ware made in transparent Vitreosil are shown in Fig. 20. These illustrate the excellent quality and workmanship of modern fused quartz apparatus.

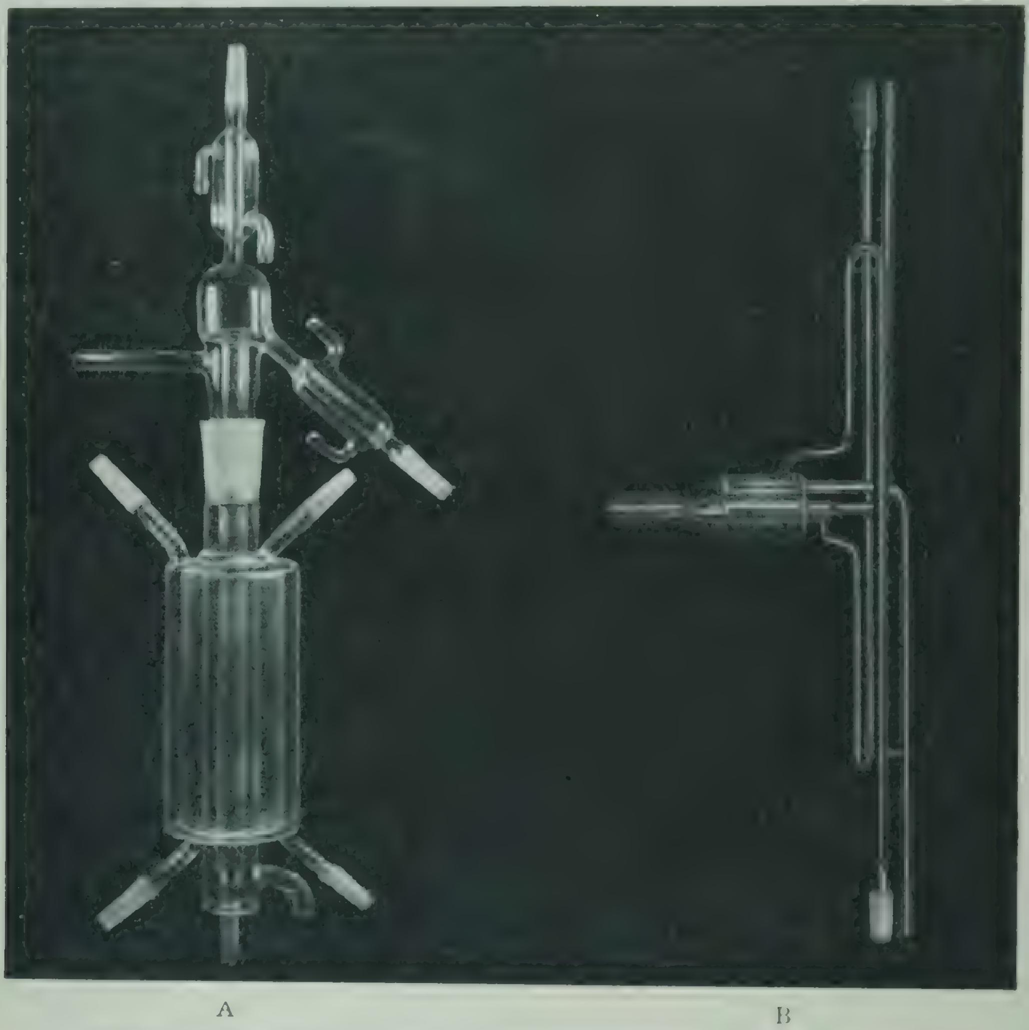


FIG. 20.—Examples of Chemical Apparatus fabricated in Fused Quartz.
(Courtesy, The Thermal Syndicate Ltd.)

Voelker's process differs from that used by the Thermal Syndicate chiefly in the construction of the furnace used; details are given in the Patent Specifications 5,764 (1907) and 18,713 (1909). The fused silica is moulded in iron moulds, a hollow cylinder with one end closed being introduced into the latter, a pellet of wet paper is dropped into the cylinder, and the open end is immediately closed by pressure. The water in the paper immediately causes the production of huge quantities of steam, which exerts sufficient pressure to make the viscous mass fill the mould.

The Quarzgesellschaft, working Voelker's patents, claimed that transparent fused silica could be produced by them under favourable conditions, though the bulk of their product was only semi-transparent and closely resembled vitreosil.

In the **Osram process** carefully selected natural quartz crystals from Brazil was broken down to nut size by quenching from 800° C. The charge was heated in an atmosphere of hydrogen and nitrogen. A molybdenum crucible in a tungsten-wound resistance furnace and the fuzed mass drawn off below through a molybdenum die.

H. J. S. Sand (British Patent, 15,629, 1913) obtains quartz glass free from bubbles by enclosing the crushed or quenched crystal in a highly evacuated envelope, and melting the whole mass in the electric furnace.

Apart from the patent specifications, the best descriptions of the various methods of fusing silica will be found in Bronn's "Elektrische Ofen in Dienste der keramischen Gewerbe und der Glas- und Quarzglaser-zeugung" (Halle, 1910).

The chief **properties** of fused silica are its complete resistance to **water, acids,** and **neutral solutions** (compare **Glass,** p. 268), the only exceptions being hydrofluoric acid and hot phosphoric acid, and their magnesium and ammonium compounds.

All **alkalis** attack fused silica, and **most metallic oxides** do so at a sufficiently high temperature.

Indeed, so sensitive is the clear fused silica to alkalis that the small proportion in human perspiration which is left by touching a clean piece of ware with the fingers and then heating to bright redness is sufficient to leave marks on the ware. For this reason, Heraeus recommends that all the ware should be rubbed with alcohol immediately before use.

Fused silica ware must not be heated in contact with asbestos, as it combines with it, but should be supported on triangles or other supports made of vitreosil.

At 1,000° C. fused silica ware becomes pervious to gases, though less so than platinum. At 1,600° C. it softens, and so is unsuitable as a container for substances to be heated above this temperature. Prolonged heating at 1,200° C. induces devitrification, especially in thin ware; short exposure to a much higher temperature will, however, do no harm in this respect.

Fused silica ware is chiefly characterised by its remarkable resistance to sudden changes in temperature; this is due to its exceptionally low coefficient of expansion. Consequently, silica ware may be made white hot and then plunged into cold water without being affected. The coefficient of expansion between 0° C. and 1,100° C. is 0.5×10^{-6}.

Thermometers made of fused silica are stated by Siebert and Kühn to be entirely free from all depression phenomena (p. 292); this is a natural consequence of the absence of metallic oxides, which, by their change of position in the less stable glasses, produce the alteration of the zero point in thermometers in which such glasses are used.

The density of the clear fused silica ware is 2.22; that of the vitreosil and similar ware is only 2.08, on account of the contained air-bubbles. Its refractive index for the D line is 1.4585 according to Abbé, and its dispersion (C–F) is 0.00676. For ultra-violet rays it is more transparent than any other glass—even than Uviol glass (p. 292)—providing that it is clear, but even a scarcely noticeable seediness renders it opaque to these rays. The use of clear fused silica ware in connection with the mercury vapour lamp by Heraeus has provided a source of ultra-violet light of remarkable intensity, and has greatly facilitated the study of photo chemical reactions, such as the formation of ozone, sulphur trioxide, hydrochloric acid, etc., from their elements.

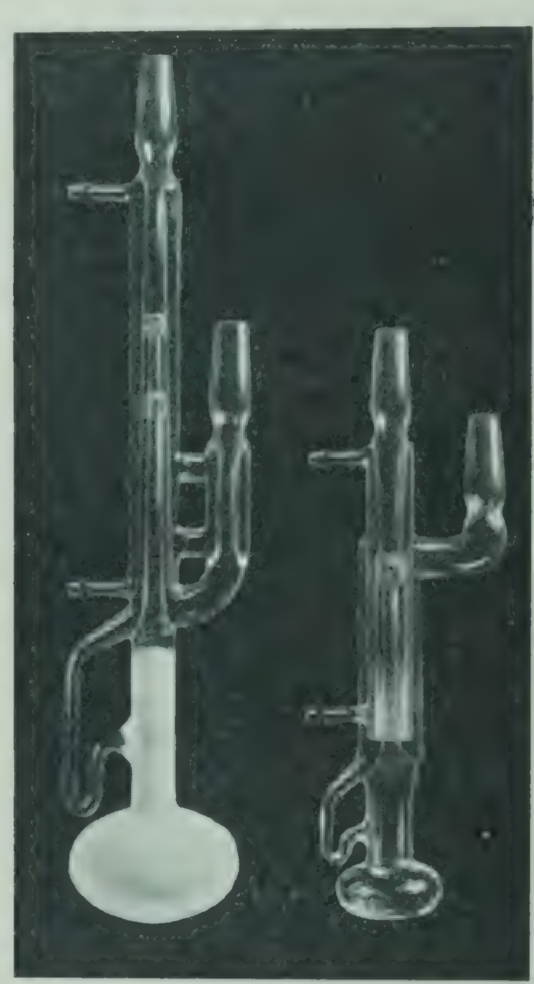


FIG. 21.—Mercury Vapour Pumps made in Vitreosil.
(Courtesy, The Thermal Syndicate Ltd.)

Mercury vapour pumps made in fused sand or quartz are now frequently used in laboratories for high vacuum work. Examples of such pumps, made of transparent and translucent Vitreosil, are shown in Fig. 21.

Optical Quartz Glass. Quartz glass of optical quality is now readily obtainable in the form of discs or plates of 20 mm. thickness and 20 cm. diameter or side, of prisms up to 7 cm. length and 10 cm. side, of lenses up to 10 cm. diameter, cuvettes or cells with plane parallel ends, etc. Down to a wavelength of *ca* 2,300 Å. quartz glass may be obtained with a lower absorption than rock crystal, but for still shorter wavelengths the latter is better. At 2,000 Å. the absorptions are 0.27 and 0.12 respectively.

REFERENCES

(1) F.I.A.T. Final Report No. 536, "Fuzed Quartz Manufacture in Germany."
(2) Zeits fur tech. Physik. "Process for the Continuous Melting and Drawing of Quartz Tubes and other High Melting Glasses." (1940).

SECTION LXXIV

ENAMELS

BY ALFRED B. SEARLE

REVISED BY MARCUS FRANCIS

LITERATURE

J. GRÜNWALD (trans. H. Hodgson).—"Enamelling on Iron and Steel." London, 1909.
—— "Iron Enamelling and Tinning." London, 1912.
—— "Raw Materials for the Enamel Industry." London, 1913.
H. M. CHAPIN.—"How to Enamel." London, 1911.
W. N. BROWN.—"Art of Enamelling." London, 1913.
—— "Principles of Dipping, Burnishing, and Lacquering." London, 1914.
J. E. HANSEN (Ed.).—"A Manual of Porcelain Enamelling." Cleveland, 1937.
—— "The Refresher Course in Porcelain Enamelling." 1945.

ENAMELS are, strictly speaking, opaque glazes, but the term is used somewhat loosely to indicate many materials which give a glossy surface to any articles to which they are applied. Thus the **japans** form one class of enamels whose basis is entirely vegetable (see "Industrial Chemistry: Organic," and the term **enamel** is extensively used with reference to a number of varnishes applied to articles with or without subsequent heat treatment. In other industries, and among those persons who are careful in the use of terms, the word enamel is only applied to substances to which a gloss is given in consequence of the particles composing the surface being heated to such a temperature that fusion has occurred, and a glass-like material formed. When used with even greater strictness, the word **enamel** relates exclusively to **opaque** substances of a glassy nature. Thus a coating of clear glass or glaze ought not to be regarded as an enamel, though much enamelled jewellery is of this kind, the metallic basis being obscured, but not hidden, by the intensity of the colour of the so-called enamel. The continual misuse of the word enamel, therefore, tends to confusion, and makes it necessary to refer to numerous substances which ought not really to be included under this title. These may be summarised as follows:—

Vegetable enamels, including lacquers and varnishes ("Industrial Chemistry: Organic").

Paint enamels, either of a cementitious character (**Sorel Cement,** p. 137), or of such a nature that they dry glossy instead of being dull.

Glassy enamels, such as are used for enamelled jewellery, etc., and consisting in reality of coloured glasses of very low melting point (highly boracic glasses).

Glazes (p. 188), which ought only to be termed enamels when they are opaque.

True enamels, or opaque glasses or glazes, made by covering the material to be enamelled with a suitable mixture, and heating both in a kiln until a glossy surface is obtained by the fusion of the glass or glaze. Such enamels are distinguished from stoved lacquers or japans by the fact that the former are of an exclusively mineral character, whilst the latter are of entirely vegetable origin. Only the true enamels are considered in what follows.

The raw ingredients of enamels are the same as those of glasses and glazes, with the addition of some opacifying medium (pp. 273 and 294). If the temperature at which the enamelling can occur is sufficiently high, opaque glasses may be used, though the difficulty of making these with precisely the same coefficient of expansion and contraction as the material to which they are applied is sometimes almost insuperable. Glazes—which are specially modified glasses—are therefore more suitable, as the constituents which they possess, in addition to those of the true glasses, are used with a view to overcoming this difficulty, a difficulty which is particularly great in the manufacture of enamelled iron ware.

The colours used in the production of enamels are the same as those used in pottery (p. 173), but as most enamelling on metal is done at relatively low temperatures it is often practicable to use a greater variety of colours than is possible for the potter, with the exception of what the latter uses in "overglaze" decoration (p. 190).

Broadly speaking, enamels are used for two distinct purposes: to improve the appearance of an article, and to give it an impervious and smooth surface. These two objects are not necessarily inseparable, so that in some cases enamels may be used for purposes of decoration (as on jewellery) which are not resistant to water, and soon decompose on exposure to wet and frost. By far the greater part of modern enamelled metal ware is made with a view to protecting the surface of the metal from the action of weather and water, and to enable the advantages of construction which are offered by iron and steel to be combined with the cleanliness and desirable surface-characteristics which are found in pottery. Much enamelled iron ware is, in fact, an attempt to produce "unbreakable pottery." Where this is the case it will be found, with few exceptions, that the true pottery is better than the enamelled ware, but in some cases pottery would appear to be unsuitable (as, for instance, enamelled iron saucepans) as it cannot be brought into direct contact with flame without being damaged. Decoratively-enamelled iron is often inartistic, and is open to the great objection that it appears to be something different from its true nature. Yet, in spite of these objections, there is an enormous field of usefulness for enamelled metal in the case of those articles where its strength, portability, and the facility with which it may be heated give it an advantage over other materials.

The **dangers** attending the use of enamelled metal for culinary purposes are seldom realised. Quite apart from the possible poisonous properties of the enamel itself—due to the use of lead compounds—there is a considerable liability to serious illness as the result of small chips of enamel becoming mixed with the food. The difference in the relative expansibility of the enamel and the metal beneath is always sufficient to cause a separation of the enamel after repeated changes in temperature. This is particularly noticeable in culinary articles, such as enamelled saucepans, and these ought not to be used when once any of the enamel has come away from the metal.

The characteristics required for enamels on pottery are practically the same as those for glazes (see p. 188).

The most important properties of enamel for iron and steel are:—

1. It must adhere well to the metal and show no tendency to leave it as by crazing (cracking) or shivering (peeling away).
2. The heat-treatment required by the ground coat and the subsequent coats must be such as to avoid the production of defects in the latter.
3. The enamel must resist the action of dilute acetic acid.
4. The enamel must contain no lead if used for domestic purposes.
5. The finished ware should have a pleasant appearance.
6. The cost of production should be sufficiently low to admit of a profit.
7. The enamel must be capable of being fired at under 1,000° C.

The production of ware covered with such enamels may be conveniently divided into four groups:—

Cast-iron (sanitary and domestic) ware.
Sheet-steel and sheet-iron ware.
Ornamental and art wares.

Cast-iron wares are usually large and heavy. The iron is rough in surface and contains numerous impurities which cause difficulties in the enamelling. Strength, with as much beauty as circumstances permit, is the chief feature.

Sheet-iron and sheet-steel wares are usually small and light; the methods by which the sheets are manufactured gives the metal a smoother surface, and the impurities in it are less objectionable. Utility and lightness are the dominant features.

Watch dials and art wares do not require to be so accurately worked, as they are not subjected to the same conditions of strain as are the sanitary and domestic wares, and for the sake of brevity they may be considered as special adaptations of the methods applied to the latter.

The enamelling of metals differs from the glazing of pottery in one very important respect, viz., the potter may vary the composition of both his body and glaze, but the metal-worker cannot materially modify the composition of the metal he is called upon to enamel. It also differs in the fact that the enamelled metals must be brought directly out of the furnace and cooled rapidly, whereas pottery may be cooled as slowly as may be desired. These differences are important, as they necessitate the whole of the permissible variations being made in the enamel itself, there being but little variation possible in the firing temperature. The composition of the enamel is, consequently, of the greatest importance, and ability to adapt it to the requirements of the manufactured articles is absolutely essential to success.

Mode of Manufacture.—The surface of the iron or steel is cleaned by means of the sand-blast (or less satisfactorily by pickling), and to the clean metal is applied a ground coat whose chief function is to form a sticky surface to which the powdered enamel will adhere until it has been fused on to the metal.

Different manufacturers have each their favourite mixtures, but their chief ingredient is borax to which sufficient clay has been added to prevent it from flowing too freely. This ground coat is applied in the form of a thick cream or slip, which is dried by gentle heat and is then fused to a somewhat rough glass. Some manufacturers prefer to fuse this coat on before applying the enamel proper, but others consider this first heating to be unnecessary. It is, of course, of the greatest importance that this ground coat should adhere perfectly to the metal, as this is its chief purpose; its appearance is of minor importance.

As soon as the ground coat is fused, the ware is withdrawn from the furnace, and before it has time to cool it is covered with the powdered enamel, applied by shaking it through a sieve of moderate fineness. The ware is again placed in the furnace and kept at the correct temperature (which usually lies between 980° and 1,000° C.) until the enamel is properly fused. If the first coating of enamel is not sufficiently thick, a second or even a third must be applied. As soon as the enamelling is completed, the ware is allowed to stand in the open workshop until cool. Muffle kilns (preferably semi-gas-fired) are invariably used; each heating takes less than ten minutes.

Materials.—The **metal** used in the enamelled sheet ware must be of high quality, as it must not only stand the necessary shaping processes, but it must be free from sulphur and phosphorus in proportions likely to affect the enamels.

It is essential that it should have a perfectly clean surface, and if oil has been used in the shaping, it will usually be necessary to heat the unglazed ware in the muffle for a short time so as to burn off all the oil and grease. If the heating is continued a little longer it will oxidise the surface of the metal, and a subsequent pickling in acid will then serve to produce a clean metallic surface.

The **enamels** are usually of a complex composition, and frequently contain all the following ingredients:—Felspar, flint, clay, chalk, sodium carbonate, borax, cryolite, felspar, saltpetre, lead, glass, and a colouring or opacifying oxide. For decorative enamels lead may be used, as its poisonous action is not generally of importance in the purposes for which these articles are used.

Two chief types of enamels are used, their composition being represented by the following "molecular formulæ":—

For cast-iron ware (sanitary ware)—

$$\left.\begin{array}{r l} 29 & \mathrm{PbO\ and\ BaO} \\ 11 & K_2O \\ 19 & Na_2O \\ 11 & CaO \\ 4 & ZnO \end{array}\right\} \quad 11\ Al_2O_3 \quad \left\{\begin{array}{l} 72\ SiO_2. \\ 14\ B_2O_3. \\ 14\ SnO_2. \end{array}\right.$$

For sheet-steel ware (domestic ware)—

$$\left.\begin{array}{r l} 7 & K_2O \\ 27 & Na_2O \\ 11 & CaO \end{array}\right\} \quad 9\ Al_2O_3 \quad \left\{\begin{array}{l} 72\ SiO_2. \\ 18\ B_2O_3. \end{array}\right.$$

In order to obtain a composition as uniform as possible it is advisable to frit (p. 162) the ingredients of the enamels and to grind the fritted mass to a fine powder. The colours are the same as those used for pottery (p. 163), the "overglaze" colours being preferred, as they agree more closely in the temperatures at which they are to be fixed. Opaque white enamels owe their characteristic appearance to the tin oxide used.

In such enamels, **soda** and **potash** may be replaced as desired, but the more potash the greater the brilliance of the enamel, as potash is almost invariably added as felspar. **Lime** appears to be essential, but too much of it makes the enamel too infusible. **Alumina** is added in the form of clay and felspar; it increases the adhesiveness of the enamel and reduces its fusibility. **Silica** is added in the form of flint, clay, and felspar; it hardens the enamel, but too little must not be used or the enamel will crack. **Fluorine** is added as cryolite, and is used to produce opacity and fusibility. **Borax** introduces both soda and boric acid; the latter behaves like silica, but it increases the fusibility of the enamel. It also increases its brilliance.

Ground Coats.—It is usually found that, providing an enamel possesses the necessary fusibility and appearance at the temperature at which the burning can be carried out, there will be little difficulty with regard to its composition. The crux of the enameller's work consists in forming a ground coat which will act as a suitable intermediary between the enamel and the metal. Indeed, this coat is the controlling factor in enamelled metal work, and where failures occur it is almost invariably due to some error in the ground coat. The two properties essential in a ground coat are (*a*) the production of an adequate bond between the metal and the enamel, and (*b*) the suitability of the fusing point. It is now agreed that the ground coat must soften at a lower temperature than the enamels applied to it, but it must not flow at as low a temperature as any of the enamels. It must, therefore, have a long range of fusion. The colour of the ground coat is unimportant; it is usually dark, on account of the metal which it dissolves from the sheet. Some workers believe that an efficient ground coat must contain cobalt, but various experiments have shown that this is not essential, though often convenient on account of the affinity between cobalt and iron.

The composition of the ground coat may be varied within wider limits than that of the covering enamels, and is more difficult to adjust to suit the requirements of any given article. Limits widely recognised are shown in the following molecular ratios:—

$$\left.\begin{array}{r l} 10—49 & K_2O \\ 0—40 & Na_2O \\ 9—42 & CaO \\ 0—4 & CoO \end{array}\right\} \quad 6—33\ Al_2O_3 \quad \left\{\begin{array}{l} 72—111\ SiO_2. \\ 13—33\ B_2O_3. \end{array}\right.$$

A composition introduced by C. H. Paris in 1850, and still extensively used, consists of broken glass, 130 parts; sodium carbonate, 20 parts; and boracic acid, 12 parts.

Tests.—The commonest test of the value of an enamel coating is to hammer it repeatedly. A really good enamel will resist many powerful blows, and where it fails it will pull off some of the steel with it. A poor enamel, on the contrary, will soon crack and peel off, leaving the clean metal below. Bending tests are sometimes tried, but they are unnatural and unfair. Heating tests—made by plunging the red-hot ware into cold water—are almost too severe, yet the best enamels will usually stand such treatment, though not repeatedly.

For domestic purposes, the ware may be tested by boiling dilute acetic acid in it. If the acid attacks the enamel, the latter will lose its gloss; the acid may also be tested to ascertain whether any lead has been dissolved from the enamel. (Strictly speaking, no lead should be used in enamel ware for culinary purposes.)

Art Enamels.—Art enamelling is almost invariably executed on gold, silver, or copper. It may be divided into four groups: **Cloisonné**, in which small divisions or cells made of fine wire are soldered on to a metal basis (usually copper), these cells being afterwards filled with powdered enamels which are fused into position; **Champlévé**, in which the design is hollowed out of a metallic surface, the hollows being filled as in cloisonné; **Limogeic**, in which the enamels are melted direct on to the base without the use of cells or hollows; **pointed enamels**, in which the enamel is dropped on to the base in a semi-molten state, in a manner similar to that used in sealing a letter with wax.

The composition of these different enamels varies greatly, but they are chiefly mixtures of flint, red lead, and nitre, with sufficient borax to give the requisite fusibility, and at the same time prevent excessive crazing or cracking. A much-used recipe for Champlévé enamel consists of—

Flint	3 parts.
Borax	1 part.
Nitre	6 parts.
Red lead	6 ,,

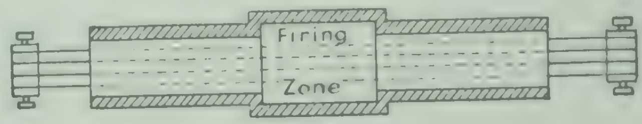
For silver enamelling, some modification of the following recipe is extensively employed—

White lead	22 parts.
Nitre	17 ,,
Flint	15 ,,

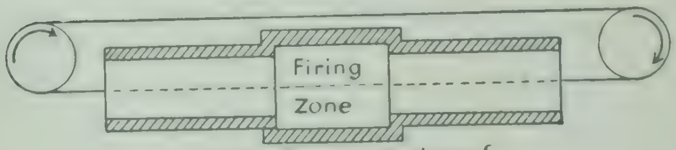
Some enamellers of gold and silver start with borax, and modify this by the addition of flint, so as to prevent crazing, but the more complex mixtures just mentioned are preferable and more durable, and correspond closely with the enamels sold ready for use.

Designs may be **painted** by hand or **printed** on paper, and transferred as in the decoration of pottery (p. 180). Sometimes the design may be printed directly on the metal, the enamel being mixed with a mixture of oil and wood tar to make it adhere.

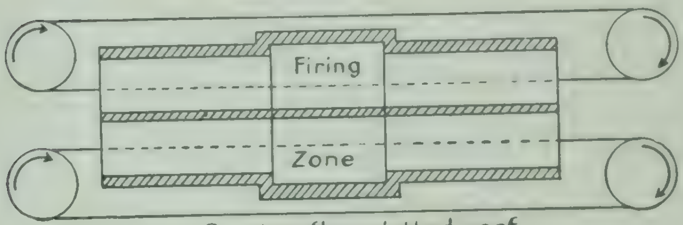
Recent Developments.—The most significant improvement in manufacture of recent years has been the introduction of continuous firing equipment. The intermittent box-furnace yielded an excellent product in skilled hands but has inherent disadvantages. In the early twenties circular semi-continuous, electrically-heated enamelling furnaces made their appearance. Later true continuous furnaces of the straight type were developed. These were of the single flow or counter-flow type (two parallel furnaces with thin dividing wall) and the goods might be conveyed through the furnace on trucks or suspended through the slotted roof from conveyor chains running overhead. The latest development is the "U" type continuous furnace which is claimed to have all the advantages and none of the disadvantages of the straight-through, slotted-roof furnace. In the



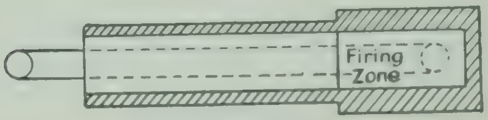
Hearth Conveyor



Single-flow slotted-roof



Counter-flow slotted-roof



"U"-type slotted-roof

Fig. 1.—Various straight types of Continuous Enamelling Furnace (after Hansen).

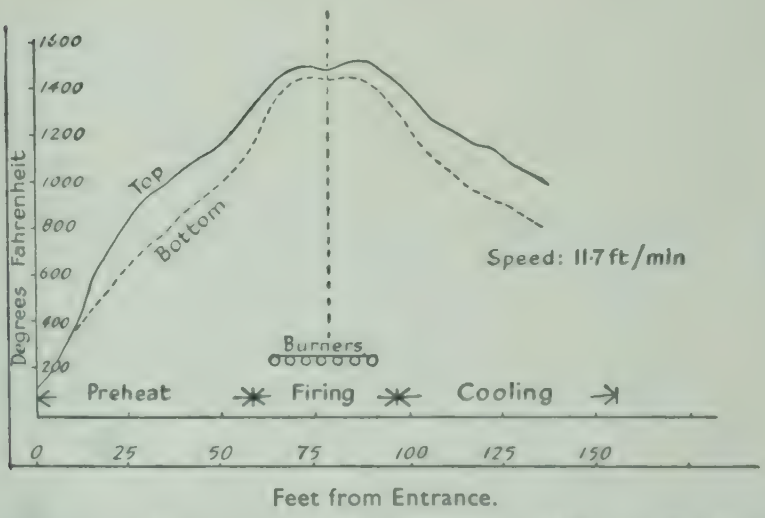


Fig. 2.—Temperature distribution and firing schedule in "U" type Continuous Furnace (after Hansen).

"U" type furnace the heated chamber is at one end, the points of entry and exit of the goods at the other. This arrangement simplifies service, the fitting into existing or new shop layouts, and the problem of quick access for cleaning out in case of accidents; it also improves thermal efficiency and heat distribution and reduces the tendency for draughts and unwanted air currents. It is adaptable to electric, oil or gas firing, to suit local conditions. The use of radiant tube burners permits the clean atmospheric conditions associated with electric heating to be obtained with the other fuels.

The different forms of furnace are illustrated diagrammatically in Fig. 1.

Improved enamel compositions and the use of continuous furnaces have made possible a reduction in firing temperatures, which are now about 100° C. lower than was formerly considered necessary. A specimen firing curve for ware fired in a "U" type continuous furnace is given in Fig. 2.

The prime cost of continuous furnaces is high but is rapidly repaid in use provided the output justifies the installation and the design is appropriate. Details of furnace operation are shown in the following table:—

PRODUCTION CAPACITIES OF ENAMELLING FURNACES.

Size or Type.	Box-Furnace, 5 ft. by 12 ft.	Continuous Furnace.	
		7 Burner.	9 Burner.
100 sq. ft./hr. of 20 ga. ware, cover-coat burn.	4–5 1 : 4 ware/supports	20–30 1 : 1 ware/supports	30–40 1 : 1 ware/supports
Cast iron, cwt./hr.	7–8 Multiple decking	30–34	40–45
Hollow-ware, 10 in. by 5 in. 100 units/hr.	5–7	20–35	35–40
Average gas consumption, 1,000 cu. ft./hr. at 550 B.Th.U.	3–3.6	6–7	8–10

Process Control.—A control laboratory is essential for the quantity production of saleable enamelled ware, though whether this should be centralised or dispersed through the various departments of the works is a matter for debate. Control should be exercised over the raw materials including water, the prepared enamels (mill room), the pickle room, the application, and the firing.

REFERENCES

(1) G. A. Hutt and P. S. Gruber, *Ceramic Bulletin*, 26, 235 (1947).

SECTION LXXV

THE ASBESTOS INDUSTRY

By Wilfrid Francis

LITERATURE

"Asbestos."—U.S. Bureau of Mines Bull. No. 403 (1937).
"Asbestos."—U.S. Bureau of Mines Inf. Circular 6817.
Asbestos.—A Magazine devoted to the Asbestos Trade. Philadelphia.
O. Bowles and D. I. Marsh.—U.S. Bur. of Mines, Minerals Year Book, 1941–46.
F.I.A.T. Final Report, No. 1070.—"Technical and Scientific Developments related to the Asbestos Industry in Germany." H.M.S.O., 1947.
S. Caillere.—*Bull. Min. France*, **59**, 163 (1936).
J. G. Ross.—"Chrysotile Asbestos in Canada." Can. Dept. Min. Bull. 707 (1931).

Definition.—The term "asbestos" is a collective name which has been applied to a variety of silicate minerals which differ from each other in chemical composition and physical properties, but resemble one another in their fine fibrous texture and flexibility. The value of these minerals largely depends on the facility with which they are capable of being split up into flexible fibres which can be spun like cotton and woven into cloth or formed into sheets or moulded compositions with the addition of organic or inorganic binders. Other criteria of commercial value are resistance to heat and chemical action.

All the useful "asbestos" of commerce can be broadly classified either as fibrous varieties of the amphibole group of minerals, or as fibrous serpentine.

AMPHIBOLE ASBESTOS

This group is of less commercial importance, since the fibres are not very suitable for textile purposes on account of the lack of strength or flexibility. They possess the advantage of being less readily attacked by acids. They usually occur closely associated with pyroxene and hornblende rocks of the crystalline metamorphic series, as aggregates or bundles of closely compacted fibres traversing the rock in crevices or veins, sometimes many feet in length. The varieties of amphibole asbestos are all relatively anhydrous compounds of silica with an alkaline earth base, and contain very little alumina. The following forms are recognised:—

1. Tremolite or Italian asbestos - $CaO.3MgO.4SiO_2$.
2. Actinolite - - - $CaO.3(Mg.Fe)O.4SiO_2$.
3. Anthophyllite - - - $6MgO.FeO.8SiO_2.H_2O$.

Tremolite and actinolite are very similar in composition, both being silicates of magnesia and lime, but the latter having some of its magnesia replaced by a molecular equivalent of ferrous iron.

The following is an analysis of typical tremolite asbestos:—

SiO_2	57.2	CaO	13.4
Al_2O_3	.9	K_2O	.3
Fe_2O_3	.5	Na_2O	.6
FeO	2.7	Loss on ignition	2.4
MgO	22.8		

They are dull green to white in colour, depending upon the amount of the iron present.

Tremolite asbestos has been mined since very ancient times in north **Italy**—Val d'Aosta and Val Tellina on the southern slopes of the Alps. Only a small percentage of the fibre can be applied to spinning, and then usually mixed with cotton. Its chief use is in the manufacture of millboard and as indurated fibre.

In **Eastern Canada** the name actinolite is apparently applied to all asbestos fibres which are wanting in flexibility, independently of their chemical composition.

Anthophyllite asbestos differs somewhat from tremolite in chemical composition, all the lime being replaced by magnesia and a part of the magnesia by ferrous iron.

A typical analysis is the following:—

SiO_2	57.4	CaO	.3
Al_2O_3	1.4	K_2O	.3
FeO	7.6	Na_2O	.6
MgO	29.5	Loss on ignition	2.6

Many of the occurrences in other parts of the world usually referred to as tremolite will prove to be anthophyllite. It is little used commercially, the fibres being brittle and usually short so that they are not generally suitable for use in textiles and are too weak to use in good quality asbestos cement. Short fibred anthophyllite is of some value as a filler for waterproofing bitumen and asphalt compositions and for magnesium oxychloride cement floorings. Some types, if carefully opened, can be used with magnesia or diatomaceous earth for the preparation of thermal insulating compositions.

Amosite is a long fibred variety of anthophyllite, containing rather high proportions of iron and occurring in South Africa. The best grades may be used for carding and spinning, but the fibre is weak and these operations are extremely dusty and not welcomed in the factory because of the additional health hazard. Consequently amosite is used mainly in moulded thermal insulating compositions, particularly that known as "85 per cent. magnesia." In this application, the long, fine, but bristly, amosite fibres form an ideal fibrous filler for the magnesia.

Crocidolite, or blue asbestos, $Na_2O.Fe_2O_3.4SiO_2 + 2FeO.SiO_2$, is a silicate of iron and soda; the following analysis shows its typical composition:—

SiO_2	52.11	MgO	1.77
Al_2O_3	1.01	CaO	.75
Fe_2O_3	20.62	Na_2O	6.16
FeO	16.75	Loss on ignition	1.58

Crocidolite is a stiffer and stronger fibre than amosite and may be used in place of chrysotile for many applications. It cannot be used for the production of the finest textiles, but is carded and spun for use in mattresses for the thermal insulation of railway engines and similar applications. Crocidolite is somewhat less soluble in acids than chrysotile and is for this reason used as yarn, cloth, or as a fibrous filling for plastics required to resist acids.

Crocidolite fuses at temperatures just above 1,000° C. and this property, together with the formation of a protective flux of reduced iron and sodium salts, makes it suitable for use in the pastes surrounding electrodes for electric welding.

Other forms of blue asbestos occur, for example in Australia and Bolivia, but these are extremely weak and cannot be used for textiles, though the fibres are long and silky in texture. Such varieties can be used as fillers for acid resisting compositions.

SERPENTINE ASBESTOS (CHRYSOTILE)

Chrysotile occurs in veins in serpentine rock, with which it is identical in composition, *i.e.*, hydrous silicate of magnesia, $3MgO.2SiO_2\,2H_2O$, with part of the magnesia often replaced by lime or ferrous oxide.

Occurrence.—Serpentine masses, with the included veins of asbestos, are to-day extensively mined in **Eastern Canada.** In the eastern townships of Quebec the asbestos occurs in certain serpentine masses, running north-east from near Lake Mephremagog for about 150 miles.

The chrysotile deposits in **South Africa** have been extensively developed, particularly those in Rhodesia, Swaziland, and the Transvaal. These deposits contain excellent spinning grades of fibre and are the source of much of the asbestos used in the asbestos industry in England.

Extensive deposits of good grade chrysotile asbestos are found in the **Ural Mountains,** and these have been developed by the U.S.S.R. In the U.S.A., chrysotile of good spinning quality occurs in Arizona and Vermont, though these deposits are not nearly so extensive as those in Quebec and Ontario. Workable deposits of chrysotile occur also in Australia, China, India, Italy, and Venezuela. These have not been operated commercially on a large scale and the demand for chrysotile asbestos of spinning qualities far exceeds the supply.

TABLE I.

WORLD PRODUCTION OF ASBESTOS, 1937–44, BY COUNTRIES, IN METRIC TONS

Country.	1937.	1938.	1939.	1940.	1941.	1942.	1943.	1944.
Argentina - - -	...	...	110	150	84	51	...	...
Australia:								
South Australia - -	123	49	46	119	152	64	11	...
Western Australia -	43	123	279	370	62	121	247	...
Canada - - - -	371,967	262,894	330,642	313,504	433,492	398,669	423,831	380,349
Cypress (exports) - -	11,892	5,668	10,377	9,673	4,874	3,503	1,332	...
Finland - - - -	7,260	...	...	...	...	...	...	...
India - - - -	102	90	266	...	372	514	59	...
Italy - - - -	6,393	6,860	...	...	...	...	...	...
Japan (approximate) -	1,000	1,000	1,000	1,000	...	...	...	...
Southern Rhodesia - -	51,722	53,352	52,900	52,518	49,191	56,546	51,149	...
Swaziland - - -	...	...	7,233	18,873	19,166	23,219	17,179	29,628
Turkey - - - -	157	668	88	99	146	295	133	...
Union of South Africa -	25,975	21,025	20,003	24,849	25,655	31,351	32,351	16,130
U.S.S.R. - - -	125,000	86,000	...	...	...	...	...	...
United States (sold or used by producers) - -	10,958	9,471	14,024	18,198	22,127	14,044	5,456	6,048

World Production of Asbestos of all types for the years 1937 to 1944, for the principle producing countries, taken from U.S. Bureau of Mines Minerals Year Book for 1944, is given in Table I.

Preparation.—Chrysotile occurs in veins varying in width from mere lines to bands or veins two or more inches across.

The veins are numerous, but they only form a small percentage of the rock mass which they occur, and therefore the mining costs are somewhat higher than for the other varieties of asbestos. This is compensated for by the greater value of the chrysotile. Normally 100 tons of rock mined yield from 3 to 4 tons of asbestos fibres of various lengths.

Since the asbestos veins are of inconstant nature and irregularly distributed throughout the serpentine masses, hence difficult to locate underground, the chrysotile is often won by open quarrying. The rock is removed with the aid of machine drills in benches or steps, and a certain amount of the crude asbestos is at once obtained by hand-cobbing direct from the vein. The fibre obtained in this way forms only a very small part of the output; the major part—in the form of smaller fibres—being separated from the serpentine by an elaborate mechanical process in which the rock is dealt with in turn by rock-breakers, driers, rotary crushers, rolls, "openers" (in which the fibres are separated from one another), fans (which remove the fibres by means of air currents), and settling chambers (in which they are collected).

The partially opened crudes are roughly separated into commercial grades, according to length and suitability for use in various industrial processes. According to the Canadian system, described more fully later, the processed fibres are classified into seven main classes, commencing with No. 1, the best spinning grade, with fibre length in excess of 1 in. and finishing with No. 7, or micro-fibre, with fibre length less than about $\frac{1}{100}$ in. The partially opened crudes may also be classified conveniently as No. 1, or best spinning grade, with fibre length $\frac{3}{4}$–$1\frac{1}{2}$ in.; No. 2, or second spinning grade, with fibre length $\frac{3}{8}$–$\frac{3}{4}$ in.; No. 3, or jointing grade, with fibre length from $\frac{1}{4}$–$\frac{5}{8}$ in. and shingle stock, suitable for use in asbestos cement, asbestos paper or millboard, and as a filler.

The technical and commercial values of asbestos depend upon fibre length and quality, or the capacity for producing well opened fibre. Prices vary greatly from time to time, but the price differential at the present time is about 600 dollars per ton for No. 1 grade to 40 dollars per ton for millboard and paper stock. Consequently, the object of all opening processes for asbestos is to preserve the length of the fibre so as to obtain the maximum proportion of the valuable longer grades of opened fibre from each grade of crude. In all cases the principle is followed of removing the opened fibre from rock or "spelks" at each stage of the crushing or beating process. In Canadian practice, the opening is accomplished by a series of gyratory crushers and "Jumbo" machines, the fibre being removed by air and is screened in each machine. The Jumbo machine is a horizontal drum, 6–8 ft. long and 24–30 ins. in diameter, in which beater arms, made of manganese steel and attached to a horizontal shaft, revolve at 400–800 r.p.m., according to the nature of the material being treated. The beaters are set at intervals of 6–8 ins. along the shaft and clear the shell of the drum by $\frac{1}{2}$–1 in. Various types of cyclone or Crighton openers are also employed in some countries. The latest machine used in England ia a "free-beating" type of machine, and in this case the fibre, carried along in an air stream, is struck by rotating arms in a series of horizontal chambers through which the material passes en route for the cyclone collector and screening devices. The principle of this machine is similar to that of the "porcupine" beater in the cotton industry, and is described fully in B.P. 533,942 (1941).

Screening and Grading.—The fibre is screened, so as to remove unopened rock and impurities, air separated, and graded at various stages in the opening processes. The types of apparatus used in these operations are either shaking screens, or vibrating screens, or trommels. Trommels are cylinders of woven-wire cloth, mounted at a small angle to the horizontal. The fibre travels down, either by the aid of paddles, or by slats fixed longitudinally, or by the rotary motion of the wire cylinder itself. The cylinder may be conveniently about 8 ft. long and 28 in. in diameter and made to revolve at 5–30 r.p.m.

Final Preparation.—Opening processes nearly always stop just before the fibre is at the optimum degree of opening for the purpose in mind, since the machines used for processing the fibre, and other materials in the manufacture of finished goods containing asbestos, always open up the fibre slightly and excess work upon the fibre is to be avoided if products with maximum strength are required.

Properties: Chrysotile is undoubtedly the most important variety of asbestos commercially, in spite of the disadvantage it possesses of being readily attacked by dilute acids. Its great value to the trade lies in the length and fineness of its silky fibres, combined with toughness, tensile strength, and extreme flexibility.

A typical analysis of chrysotile asbestos is the following:—

SiO_2	41.50
Al_2O_3	1.11
FeO	1.83
MgO	41.06
Combined water	14.37
	99.87

USES OF ASBESTOS

Both **amphibole** and **chrysotile** asbestos have their own uses, for which each is well adapted, though the demand for the latter is always much greater than for the former.

Thus the stability towards acids of **tremolite** and **actinolite** asbestos enables them to be used as a filtering material for these corrosive liquids; their good fire-resisting qualities render them quite suitable for use in gas fires. In the manufacture of fireproof objects for the protection of life and property (such as fireproof curtains for theatres, clothing for firemen, ropes for escape from burning buildings, etc.) **chrysotile** is employed, since tremolite and actinolite asbestos are not sufficiently flexible to be woven, and crocidolite much too fusible. In its extensive employment as a non-conductor of heat, the stability towards heat of asbestos gives it an advantage over other substances—except mica and diatomaceous earth.

The following are the main commercial uses of asbestos; under each is given a brief account of the manufacturing processes involved:—

Asbestos Textiles.—These are made from chrysotile, or crocidolite, and include yarn, rope, tape, cloth, and felts. In the "grey" condition these textiles are used mainly for fire-fighting, insulation, protective clothing, and packings; whilst, impregnated with various organic or inorganic plastics, the textiles are used for a wide variety of industrial applications, some of which are given below.

In the manufacture of textiles, only the longer grades of fibre are used. The opened fibre is first "carded" in revolving cylinder carding machines, such as are used in the waste woollen industry, usually blended with from 5 to 15 per cent. of cotton. The "sliver" so produced is then spun into yarn on spinning frames, or is sometimes used as such for winding round wires or for twisting into insulating rope. The yarn may be used, as such, for a variety of applications, for example as sewing thread for asbestos goods or for winding round wires for insulating purposes. The bulk of the yarn produced is, however, used for the manufacture of asbestos tape, braid, or cloth. Asbestos textiles are always coarse in comparison with organic textiles, but they form the ideal medium for impregnated fibrous products, because of the large number of small air spaces that they contain and the ease with which the asbestos blends with many of the impregnants used commercially. Asbestos textiles, in the grey state or impregnated, may be calendered readily without damage, which enables them to resist competition from glass fibre products in fields where these two inorganic textiles compete.

Packing Materials.—Gland and valve packings and heat and chemical resistant gaskets are required in all machines and industrial plants. Asbestos textiles form an ideal medium for these products and a large proportion of the asbestos textiles produced find their way into such applications. For gland and valve packings, asbestos fibre, yarn, tape, or cloth is impregnated with a lubricating paste and then wound or twisted into the desired shape or form. Frequently rubber is used for proofing, or as an insert into special types of packings, and the product may be supplied in vulcanised or unvulcanised form. For liquid, chemical, or heat-resisting gaskets, short asbestos, usually grade 2 or 3, is mixed with a solution or emulsion of rubber or other plastic, and then sheeted out on to the hot bowl of a calender, where the solvent is evaporated, and the rubber cured when a vulcanised jointing is required. The well-known "Klingerit" jointings are made in this way.

Resin-Bonded Asbestos Products.—Asbestos blends readily with phenol and cresol formaldehyde resins to form sheet or moulded products of great commercial importance. Asbestos textiles in the form of sliver, yarn, tape, braid, felt, or cloth, made from either chrysotile or crocidolite, are readily impregnated with these resins and, when cured under pressure, the products may be considerably stronger and have greater resistance to heat, moisture, and chemicals than corresponding products made from other fibrous fillers. The well-known brand of products known as "Ferobestos" are illustrations of this point. Sheet or board products may also be made by impregnating asbestos paper or millboard with resins, but such products are always inferior to corresponding products made from asbestos textiles. Brake linings, in which oil-modified resins may be used, are an important application of resin bonded asbestos products.

Thermal Insulating Compositions.—Asbestos is used alone, in fibrous or textile form, as a thermal insulating medium, or it is used as a filler in various insulating compositions, particularly with light magnesia as 85 per cent. magnesia and with diatomaceous earth and adhesives in moulded or plastic compositions. An ingenious device for spraying thermal and sound-insulating compositions on to buildings or equipment is described in B.P. 368,368 (1932) and B.P. 583,077 (1946). Table II shows the thermal properties of asbestos insulating compositions in comparison with other competitive materials.

TABLE II

THERMAL CONDUCTIVITIES OF CERTAIN INSULATING MATERIALS

Mean Temp. °F.	Conductivity in B.Th.U./sq. ft./hr./°F./in.						
	Hair Felt.	Asbestos Sections.	85 per cent. Magnesia.	Spun glass Sections.	Slag Wool.	Steel Wool.	Aluminium Wool.
50	0.29	...	...	...	...	...	...
100	0.33	0.41	0.405	0.30	0.36	0.45	0.735
200	...	0.46	0.45	0.36	0.45	0.66	1.08
300	...	0.52	0.49	0.45	...	0.895	1.41
400	...	0.585	0.54	0.58	0.58	1.11	...
500	...	...	0.59	0.76	...	1.32	...

Asbestos Paper and Millboard.—Short asbestos fibre may be sheeted out on ordinary paper- or board-making machines without the addition of organic fibres, though sometimes sulphite pulp, or other organic paper-making stock, is added to assist the operation or to increase the strength of the product. Asbestos paper is used for a variety of insulating purposes and, when impregnated with bitumen, forms a valuable roofing felt or damp course material.

Asbestos Cement.—The greatest tonnage of asbestos used in the world to-day is in the form of asbestos cement. When short asbestos fibres are mixed in a thin slurry with a large proportion of Portland cement, the product may be sheeted out on a board-making machine, or on a special machine in which thin layers of the mix are first picked up on a felt, and then transferred on to a forming bowl until the desired thickness is built up. When sheeted out, the wet mix may be handled readily and formed into corrugated sheets, hoods, ducts, cowls, and a variety of useful shapes for constructional use. The wet mix has a "bench" life of several hours, and cures to a hard product in a few days at ordinary temperatures.

The product is too well known to describe, but it has supplied the long-felt want for a cheap, reliable, inorganic sheet material for building purposes. Several Standard Specifications have been issued in different countries recently to cover asbestos cement goods.(5)

The normal composition of asbestos cement is $12\frac{1}{2}$ per cent. to 15 per cent. of short asbestos, and $87\frac{1}{2}$ per cent. to 85 per cent. of Portland cement. Occasionally other proportions are used, but the extreme range is from about 10 per cent. of asbestos to 25 per cent.

Grading and Classification.—The Canadian Standard method of testing and grading asbestos fibres, taken from the publication by Ross mentioned in the literature, is as follows:—

The machine consists of a nest of four wooden boxes measuring $24\frac{1}{2}$ by $14\frac{3}{4}$ in. and $3\frac{1}{2}$ in. in depth. The boxes, which are superposed one above the other, are numbered, from the top down, 1, 2, 3, and 4. The bottoms of boxes 1, 2, and 3 are made of metallic screen of the following specifications: Box 1: $\frac{1}{2}$-in. opening, diameter of wire, 0.105 in. Box 2: 4-mesh wire, 0.063 in. Box 3: 10-mesh wire, 0.047 in. Box 4 is a receptacle for the fines that fall through the three other boxes. The nest of four boxes or trays rests on a table to which an eccentric with a throw of $\frac{25}{32}$ in. gives a movement of $1\frac{9}{16}$ in. travel.

To make a test, 16 oz. of asbestos is put on the top tray, which is covered. The machine is run at the rate of 300 r.p.m. at the shaft of the eccentric, and by means of an automatic device this is kept going for exactly 2 minutes, giving the nest a horizontal shaking movement. At the end of this time the asbestos that remains on each tray is weighed. This gives the grades of the asbestos fibre; the longest fibre naturally stays on the top tray, whereas the shorter fibre, according to its length, remains on screens 2 and 3 or drops into the pan or lowest tray. The more fibre retained on the first screen and the less fibre in the pan, the higher the grade and, therefore, the greater its value. If, for instance, a customer buys spinning fibre of the specification 4–7–4–1, it means that in a sample of 16 oz., representing the average of the lot shipped, 4 oz. will remain on the top screen, 7 on the second, 4 on the third, and, finally, 1 oz. will go through all the screens into the pan.

For a complete description of the grades of milled asbestos and the sub-division of these grades, see the publication by Ross (*loc. cit.*) or U.S. Bureau of Mines Bulletin No. 403.

Health Hazards.—The asbestos industry is, unfortunately, associated with a dangerous hazard, somewhat related to silicosis, known as asbestosis. Before the dangers were realised, about the year 1925, many workers in the industry were injured or killed by this disease. Asbestosis is a form of pneumoconiosis and is caused by fine fibres of asbestos lodging in the capillaries of the lungs and irritating the soft tissues opposite, as they move during breathing. The fibres become covered with congealed products of the irritation and they are then known as "asbestosis bodies." These cause congestion of the lungs and death is often accelerated by tuberculosis or other lung complaints. Since the recognition of this hazard, efficient ventilation of asbestos textile factories has done much to reduce its incidence, whilst, by frequent medical examination of the workers, and removal from contact with dust at the first signs of trouble, the death-rate due to these causes has been greatly diminished in recent years.

REFERENCES

(1) O. Bowles, *Min. Met. Eng.*, October 1938.
(2) J. G. Ross and G. F. Jenkins, *Ind. Min. and Rocks*, *Am. Inst. Min. Met. Eng.*, 75 (1937).
(3) D. Wolochow, *Can. Min. Met. Bull.* (1938).
(4) W. Francis and J. Grayson, *J.S.C.I.*, LX, 160 (1941).
(5) B.S. No. 690, "Asbestos Cement Slates and Sheets" (1945).

SECTION LXXVI

THE MICA INDUSTRY

By F. W. Penny, B.Sc., F.G.S.

Revised by Wilfrid Francis

LITERATURE

Adams and Barlow.—Memoir No. 6, Geol. Survey, Canada, 1910.
Schmidt.—"Mica." Report No. 118, Canadian Dep. of Mines, 1912.
B.I.O.S. 785.—"The German Mica Industry." 1946.
F.I.A.T. 746.—"Synthetic Mica Industry." 1946.
U.S. National Bureau of Standards.—"Synthetic Mica." *Technical News Bulletin*, **34**, No. 2, 20 (1950).

Occurrence.—Mica is one of the most widely distributed of minerals. It occurs in the form of small scales and plates in the majority of igneous and metamorphic rocks and in many of the products formed from their decomposition. However, mica of commerce is practically confined to three of these varieties—**muscovite, phlogopite,** and **biotite**.

Large plates of **muscovite** are almost entirely restricted to those dykes or veins known as **pegmatite** which are usually associated with great granite masses. The commercially valuable mica occurs in rough tabular or tapering six-sided crystals known as "books," from the facility with which they can be opened up into thin leaves; they vary from a few inches up to several feet in diameter.

Muscovite has been worked principally in India and the United States.

From Eastern Canada comes the world's supply of **phlogopite** mica, which has quite a different genesis. It occurs associated with dykes of basic rock, generally pyroxenites. The mica occurs quite irregularly in pockets, sometimes joined by narrow fissures having no definite direction.

Owing to the impersistent nature of mica deposits, there are few rules or indications by which the miner may be guided. But the mica found at the surface is nearly always soft and cracked, due to the action of weathering and surface movements; clearer and better coloured mineral is found lower down in the solid rock, *i.e.*, the quality improves with the depth.

Species of Mica.—The term mica includes a number of allied mineral substances which are characterised by great fissibility, high flexibility, and elasticity in thin films, a hardness of from 2 to 3 (capable of just being scratched with a dry finger-nail), and transparency when in thin plates. The principal species of commercial importance are:—

(*a*) **Muscovite,** or potash-aluminium mica: composition normally—

$$Al_3KH_2Si_3O_{12}[3Al_2O_3.K_2O.6SiO_2.2H_2O];$$

specific gravity, 2.85.

Typical analyses give the following as the average percentage composition of this species:—

Silica, SiO_2	45 to 47 per cent.
Alumina, Al_2O_3	30 ,, 37 ,,
Ferric oxide, Fe_2O_3	0.5 ,, 5 ,,
Ferrous oxide, FeO	0.5 ,, 2 ,,
Magnesia, MgO	0 ,, 2 ,,
Potash, K_2O	8 ,, 11 ,,
Soda, Na_2O	0 ,, 2 ,,
Water, H_2O	4 ,, 6 ,,
Fluorine, F	0 ,, 1 ,,

If the percentage of the iron oxides rises above 5, muscovite becomes distinctly tinted when plates thicker than 0.5 mm. (0.02 in.) are viewed by transmitted light.

(*b*) **Phlogopite,** or magnesia mica, approximates to—

$$AlMg_3KH_2Si_3O_{12}[Al_2O_3.6MgO.K_2O.6SiO_2.2H_2O];$$

usually contains some fluorine; specific gravity, 2.75.

The percentage composition is usually within the following limits:—

Silica, SiO_2	39 to 44 per cent.
Alumina, Al_2O_3	13 ,, 15 ,,
Ferric oxide, Fe_2O_3	0 ,, 2 ,,
Ferrous oxide, FeO	0 ,, 1.5 ,,
Magnesia, MgO	26 ,, 29 ,,
Potash, K_2O	8 ,, 10 ,,
Soda, Na_2O	0.4 ,, 2 ,,
Water, H_2O	1 ,, 5 ,,
Fluorine, F	1 ,, 5 ,,

As a rule, phlogopite is coloured more deeply than muscovite by the presence of the same proportion of iron oxides. When the total amount exceeds 5 per cent., a plate only 0.1 mm. (.004 in.) thick is distinctly tinted. When the percentage of iron is under 2, the phlogopite shows a pale yellow colour in a thickness of 0.1–0.5 mm., the colour passing to an amber shade with thicker plates. This is the variety known to the trade as **amber mica.**

(*c*) **Lepidolite,** a lithia-bearing mica of variable composition, in most cases a mixture of a fluoriferous trisilicate, $AlF_2.Si_3O_8.R'_3$ (in which $R'' = Li_1K$), with molecules of the muscovite type. It is characteristically of a pink or mauve tinge.

It has a very limited use for the production of lithium salts, largely used in the manufacture of lithia water since it contains theoretically about 4 per cent. of lithium.

It is important to be able to distinguish phlogopite from muscovite, and this is easily done with a polarising or petrological microscope. A plate should be peeled until it is as nearly as possible 0.25 mm. (0.01 in.) in thickness; it should then be rotated between crossed nicols. A plate of muscovite under these conditions shows bright colours, whilst one of phlogopite allows only a faint greyish-white light to pass.

(*d*) **Biotite**, a brown ferro-magnesium variety of the approximate composition $H_2K(Mg,Fe)_3(Al.Fe)(SiO_4)_3$.

This is rarely used in sheet form since it is frequently contaminated with iron containing impurities. Its normal use, in powdered form, is a coating or filler in the roofing, flooring, rubber and building trades.

Manufacture. Mica is usually exploited by open quarrying, waste rock being loosened by very light blasting (hand drilled holes not more than 4 ft. deep and charged with ordinary powder), and the crystals being taken out with crowbars and chisels.

In a typical Canadian mine about 150 ft. deep the cost of producing a ton of mica from 1 × 3 in. in size upwards was about £35 per ton under pre-war conditions.

The rough crystals have first to be split into sheets $\frac{1}{8}$–$\frac{1}{16}$ in. in thickness, done by hand with short-handled knives, and at the same time all loose and broken edges are torn off with the thumb and forefinger, a process known as "thumb-trimming." The thumb-trimmed sheets are next cut by hand machines—usually at special works—into rectangular form, so as to yield the largest superficial sizes whilst avoiding all striations, marginal cracks, and other faults. Plates which are broken, unevenly laminated, striated, crumpled, cracked, or much stained are useless, and should be discarded.

As a general rule not 10 per cent. of the mica mined is capable of being cut into sound rectangular plates of size not less than 2 × 3 in. or 4 × 1 in., which are about the economic size-limit. In Canada it is reckoned that 3 tons of scrap mica, yielding 750 lbs. of thumb-trimmed material, must be raised for every 100 tons of rock removed from open quarries; for underground mining (up to 300 ft. deep) 5 tons, yielding 1,250 lbs. of thumb-trimmed mica, must be extracted to make it pay.

The balance of scrap or waste mica is sold for conversion into **ground mica.**

The operation of grinding mica to a fine powder is a rather difficult one to carry out owing to the fact that the mineral has a single perfect cleavage, and cleavage-lamellæ are very smooth, tough, and elastic. In most cases the details of the processes are kept secret, but a certain amount of information can be obtained from Schmidt, *loc. cit.*, pp. 307 *sqq*. The fineness required for industrial purposes is up to 160 meshes to the inch.

Uses.—The uses of **sheet** mica can roughly be divided into two classes, the first comprising those for which a substance is required that is transparent and impervious to heat—for lamp chimneys, furnace windows, etc.—and the second consisting of those connected with the construction of electrical machinery. For the former purposes **muscovite** is generally employed, since the material must be clear and transparent. The best kinds show a faint ruby tint in plates approaching a millimetre (.04 in.) in thickness; the plane of cleavage must be quite true and it must be perfectly fissile, films 0.01 mm. (.004 in.) being produced without much difficulty. It must be flexible and elastic in fairly thin laminæ; for instance, a plate 0.01 mm. thick would bend without cracking or appreciable buckling round a cylinder 25 mm. (1 in.) in diameter, and on being released after half a minute should regain as nearly as possible its original plane surface. The lustre must be "splendent," that is to say equal to that of highly polished glass. The standard sizes for the purposes stated above range from $1\frac{1}{2}$ × 2 in. to 8 × 10 in.: smaller sizes seldom pay for mining and preparation.

Formerly the chief value of mica was for this class of work, but recently a number of very resistant glasses have been put upon the market and these tend to restrict its use in these directions. However, by far the most important use of mica nowadays is in the construction of electrical machinery.

Phlogopite has here been found to be the most satisfactory form on account of its incombustible and insulating powers and also because of the fact that for the construction of commutators of direct-current motors and dynamos (which are built up of bars of copper and strips of mica) the phlogopite has about the same hardness as the copper of the commutator segments, and therefore wears down evenly without causing the machine to spark.

The colour of the sheets is of little moment, but very dark mica is not likely to be of much value owing to the iron it contains rendering it useless for insulating purposes, a fairly low percentage of iron being an essential for the latter. Perfect cleavage is of the highest importance, as "electric mica" must be of uniform thickness and is often gauged to the one thousandth part of an inch. The sheets must be absolutely free from cracks, for it is obvious that even microscopic cracks would militate against a material being used as an electric insulator. Lastly, a perfectly flat surface must be secured on splitting the mica into sheets, as mica with "metallic insertions" or "hydration lumps" is useless for insulating.

The sizes most favoured are 2 × 4 in. and 1 × 3 in., or long strips up to 1 × 6 in., but there is nowadays a big demand also for the smaller sized sheets (1 × 1 in. and 1 × 2 in.) for the purpose of making **micanite,** a material built up of small and inexpensive plates about .005 in. in thickness, with an insulating cement such as shellac to form non-conducting sheets on a foundation of longcloth or paper, the made-up material being finally subjected to great pressure under heat to dry out the shellac.

Lastly, a large variety of uses have been found for the **ground mica**—the finer grades (160 mesh) of muscovite can be mixed with a solution of gum arabic for making a good silver paint; or for producing bronze-like colours which are lighter than metallic bronzes and are not so liable to be tarnished; also for imparting a lustrous appearance to wall-papers, etc. Mixed with shellac or special compounds, the coarser grades can be moulded into desired forms and find employment as insulators for wires carrying high-potential currents: for this purpose the ground mica must be rendered free from metallic particles. It is used in combination with grease, graphite, or oils as a lubricant for axles and other bearings—for which purpose it must be freed from gritty matter. Another application is its use in place of kieselguhr as an absorbent of nitro-glycerine, the explosive thus formed being known as **mica powder.** But probably a more important use, in connection with scrap mica, is as a non-conductor of heat, especially for packing, and jackets for boilers and steam-pipes, since it will stand any abnormal heating, is practically free from moisture and acids which attack iron and steel, and if moisture leaks in, the mineral is completely unaffected by it.

Production.—The demand for larger mica has increased steadily for some years with the advance of electrical requirements. On the other hand, the supply from some of the older localities (Madras) is decreasing owing to the depth to which the mines have already been worked. Localities where in past geological ages the special conditions requisite for the formation of large and uncracked crystals of suitable mica existed are of limited occurrence, and new ones are not being quickly discovered.

The chief mica-producing countries at the present day are India, Canada, and the United States.

In **India** the production comes mainly from the Hazaribagh district of Bengal (57 per cent.) and the Nellore district of Madras (31 per cent.). The mica mined is exclusively muscovite, and the following are the principal classes recognised:—

"**Bengal Ruby**" and "**Madras Ruby,**" the latter not having such a good plane of cleavage, but greater fissibility than the former.

"**Bengal Yellow,**" less common, but equally valuable.

"**Madras Green Clear,**" liable to crack when manipulated.

"**Bengal White,**" "mealy," *i.e.*, cloudy from incipient decomposition or interlamellar inclusion of gas; it is softer than the ruby mica.

"**Madras Green Hydrated**" is softer than the ordinary green mica from that place.

From **Canada** comes **phlogopite mica,** usually amber-coloured, rarely colourless in thin plates. Since it is used mostly for electrical purposes, the amount of colour is not important, though the darkest varieties are as a rule poor splitters. The best kinds are classified into "**light amber,**" "**dark amber,**" and "**silver amber,**" the latter being the predominant quality produced. The lightest-coloured varieties are not favourably regarded, being as a rule more brittle and less elastic than the "silver amber" mica.

PRODUCTION OF MICA—PRINCIPAL COUNTRIES *
Tons

Country and Type of Mica.	1938.	1947.
Union of South Africa (chiefly scrap)	1,098	1,975
S. Rhodesia	...	291
Canada (chiefly phlogopite)	463	3,714
India (muscovite)—		
Blocks	942	680†
Splittings	4,713	6,890†
Scrap	3,101	1,419†
Madagascar	667	444
U.S.A.—		
Sheets	419	186
Scrap	18,087	44,462
Argentina	263	...
Brazil	513	843
U.S.S.R.	9,000‡	9,000‡

* Abstracted from "The Mineral Industry," Imperial Institute, London, 1949.
† January to November, only. ‡ Estimated.

Value.—The micas of commerce are usually divided into three qualities for valuation purposes: "clear"—being quite free from spots; "slightly stained"—having, say, one or two stains in four square inches, and "stained" or "spotted." It has been stated that "slightly stained" mica is worth about half the price of "clear," other things being equal; and the "stained," a quarter in the case of small plates and an eighth in the case of large plates.

Vermiculite is an impure form of biotite mica consisting of a hydrated ferrous-aluminium-magnesium silicate of variable composition. Its outstanding characteristic is that, on heating, the evolution of water within the lattice planes causes a considerable expansion in volume, without complete disruption of the solid structure. This property of exfoliation, during which the best material expands from 10 to 20 times the original volume, produces a light-weight insulating material weighing from 5 to 10 lb. per cubic ft. Consequently, the exfoliated material has been used extensively in recent years for the production of sound and heat insulating plastics and lagging compositions. The larger sized material is also used for thermal insulation, as a filling for partitions of buildings or refrigerators, or as an insulating layer over the ceilings of rooms. When mixed with Portland cement, it can be made into pre-cast, light-weight, fire-proof slabs or partitions, or can be poured in place or plastered on to walls.

The material is also of value after exfoliation as an ingredient of compost in horticulture, in hydropower, and the lighter varieties are used in translucent or light-reflecting finishes for wall-paper and similar applications.

The largest vermiculite deposits are in Montana, U.S.A., though it is also found extensively in parts of Africa, including the Transvaal, in Egypt, Tanganyika, and the Urals. Production in the U.S.A. alone reached a value of nearly 100,000 tons during 1939.

Synthetic Mica.—Synthetic mica, with essentially the same properties as natural mica, but able to withstand much higher temperatures, has now been crystallized successfully at the National Bureau of Standards in the U.S.A. The following is an abstract of the paper on "Synthetic Mica," taken from the *News Bulletin* of the Bureau quoted in the literature:—

"The raw materials for making synthetic mica are similar to the raw materials sometimes used in making glass: *i.e.*, quartz, magnesite, bauxite, and a fluorosilicate compound (the only unusual ingredient). The raw mixture is placed in a platinum-lined crucible and melted in an electric furnace at a temperature of nearly 1,400° C. As the furnace cools, mica crystals grow from a tiny seed at the bottom of the crucible.

"The most satisfactory synthetic mica developed so far has the chemical formula, $K_4Mg_{12}Al_3Si_{12}O_{40}F_8$. This is equivalent to a form of natural mica in which the hydroxyl radical has been replaced by fluorine. Impurities may occur in the synthetic mica in the form of milky films parallel to the individual layers, or white patches between crystals. Crystals free of impurities are clear and transparent, and thin flakes are easily split away along the planes of natural cleavage. The synthetic form has physical properties that compare favourably with natural mica. Electrical measurements on several clear flakes, $\frac{3}{4}$ in. square by $\frac{1}{32}$ in. thick, indicate a dielectric constant of about 6.3. The largest crystals grown so far at the National Bureau of Standards have a surface area of 4 sq. in.

"Satisfactory mica synthesis depends to a large extent on the materials used in the crucible lining. Ceramic linings are badly corroded by a fluorine-bearing melt. Carbon and silicon carbide crucibles are somewhat better, but fluoride gases escape through the relatively porous walls, and fine carbon particles become imbedded throughout the synthesized mica. Crucibles lined with platinum foil give the best results. They do not react with the melt and are able to withstand high temperatures for long periods. Although initial cost is high, the platinum linings may be melted down and reformed again and again.

"The shape of the crucible is also important in mica synthesis. Flat-bottomed crucibles are not desirable, because they offer a large surface for the formation of many seed crystals that grow independently in different directions and thus limit the development of single large crystals. Mica has a sheetlike structure and grows faster in a direction parallel to its cleavage plane than in any other direction. Consequently, if a crucible with a cone-shaped bottom is used, the number of seed crystals is reduced and the direction of growth tends to be upward. Experiments are now in progress to find ways of predetermining crystal growth even more completely in order to grow large parallel sheets. The key to this seems to be precise control of temperature differences within the crucible.

"The United States is the world's largest consumer of natural mica, but it produces only enough to meet a third of its requirements. During 1948 the United States imported over 10,000 tons of high-grade mica, mostly from India and Brazil, valued at more than 15 million dollars; in the same period, domestic high-grade production totalled only 135 tons, with a value of less than 50,000 dollars.

"Since the war, world production of natural sheet mica has declined sharply, while production of ground mica has shown a continuing rise to meet the needs of roofing, paint, and rubber industries. The drop in sheet mica output reflects not only decreasing military demands for high-grade mica but also increasing labour costs, which make hand-processing unprofitable. The usable sheet product is only a small fraction of the total processed volume. Some foreign countries can still process natural mica cheaply by hand methods, but producers in the United States are now concentrating on the production of 'half-trim' mica.

"Successful control of crystal orientation in the growth of synthetic mica would mean that machine methods could be used for large-scale domestic production of sheet mica. In this way mica synthesis could make the United States self-sufficient in high-grade mica insulating materials."

SECTION LXXVII

THE THORIUM AND CERIUM INDUSTRIES

By Norbert Berkowitz

PART I—THORIUM

LITERATURE

P. Pascal.—"Traité de Chimie Minérale," Vol. XI, 1932.

J. W. Mellor.—"Textbook of Theoretical and Inorganic Chemistry."

S. Iimori.—"The Uranium-Thorium ratio in Monazites." *Tokio Inst. Phys. and Chem. Res., Sci. Papers*, Vol. X, 1929.

H. H. Helmick.—"Determination of Thorium in Monazite Sand by an Emanation Method." Diss., Univ. Chicago, 1922.

J. H. Coste and W. E. F. Powney.—"The Testing of Incandescent Mantles." *J. Chem. Soc. Ind.*, **30**, 65 (1911).

B.I.O.S. 276.—"Thorium Metal, Zirconium and other Special Metals; Special Getters."

THORIUM

Thorium (Th; atomic weight = 232.12; atomic number = 90) is probably the best known member of the rare earth group of metals. Its oxide, **thoria** (ThO_2), was discovered in 1828 by Berzelius, who isolated it from a mineral now known as thorite, and this began to find industrial application with the invention of the incandescent gas mantle by Auer von Welsbach in 1885.

Natural Occurrence.—Up to about 1890, thorium was mainly obtained from rare earth minerals, such as **thorite** ($ThSiO_4$), **samarskite** (a mixed oxide of iron, calcium, uranium, cerium, and yttrium group metals), and **gadolinite** (a silicate of beryllium, iron, and yttrium group metals). These minerals, however, although widely distributed, generally only occur in small quantities (notably in Norway and Sweden), and are difficult to obtain economically.

In modern practice, therefore, thorium is mainly extracted from **monazite.** This substance—which is essentially a phosphate of the cerium group metals—is an accessory mineral in granites, pegmatites, and gneisses, and occurs in workable concentrations in detrital **monazite sand.** Probably the most extensive deposits of this sand are located along the Brazilian coast, particularly near Bahia, Espirito Santo, and Rio de Janeiro. At these localities, monazite occurs in the form of fine grains (usually less than 1 millimeter in diameter), in concentrations varying between about 2 and 60 per cent. Large deposits of monazite sand have also been reported from the Brazilian interior, but these do not so far appear to have been exploited on a substantial scale; preliminary drilling programmes have, however, been undertaken, and these have indicated that monazite is to be found in 4–6 ft. thick gravel beds to the extent of 2–4 per cent.

Elsewhere, workable deposits of monazite occur in North and South Carolina (U.S.A.), in the Transvaal province of South Africa, and in Ceylon, Nigeria, Nyasaland, Travancore, and the Malay States. Smaller accumulations are also worked in the Ilmen mountain district of Russia and in Norway. The **thorium contents** of monazites from different localities vary between fairly wide limits.

For example, Ceylon monazite may carry between 9.5 and 11 per cent. ThO_2; Nigerian monazite between 2.3 and 8 per cent.; Malayan monazite between 3.4 and 9.4 per cent.; and Brazilian monazite between 6.1 and 6.5 per cent. The bulk of the balance is in all cases made up of the oxides of cerium and lanthanum group metals, and of phosphoric acid. The ceria contents generally lie around 30 per cent.

Of the other thorium minerals (of which some 14 have so far been described), only **thorite** ($ThSiO_4$) and **thorianite** (a mixture of thorium and uranium oxides) are still occasionally used as sources of thorium.

Thorite ($ThSiO_4$), similar to zircon in form and structure, has a hardness of 4.5–5 and a specific gravity of 4.5–5.0. It is usually hydrated and black in colour. (An orange variety, known as **orangite**, has also been reported, but this is comparatively rare.) Thorite is found mainly in Norway and Sweden (from where orangite and a uranium-bearing thorite—**uranothorite**—have also been obtained) and at various localities in Madagascar. Some typical analyses of thorite are reproduced in Table I.

TABLE I

ANALYSES OF THORITE AND ORANGITE

Source.	SiO_2.	ThO_2.	U_2O_3.	PbO.	Fe_2O_3.	CaO.	H_2O.
Norway—							
Lovo	19.31	58.91	1.64	0.82	3.46	2.62	9.66
Brevig	17.69	71.25	...	...	0.31	2.24	6.90
Arendal	17.62	69.92	1.09	...	1.23	1.07	7.01
Asia Minor—							
Batum	16.55	68.71	1.20	0.90	0.30	2.30	6.43
Ceylon—							
Kondrugala	14.10	66.26	0.46	...	1.71	0.35	6.40
U.S.A.—							
Champlain, N.Y.	19.38	52.07	9.96	0.40	4.01	2.34	11.31
Norway—							
Arendal	17.04	50.06	9.78	1.67	7.60	1.99	9.40
Brevig	17.00	50.05	9.67	0.36	7.82	0.36	11.95

Note.—The last three specimens are samples of *urano*-thorite.

Thorianite has a hardness of 6.5 and a specific gravity of 9.3, is invariably black and very nearly opaque. It has been obtained from the gem gravels of Balangoda (Ceylon), and has also been found near Betroka in Madagascar.

For the composition of thorianite see Table II below.

TABLE II

COMPOSITION OF TYPICAL THORIANITE

Component.	Percentage.
Silica	Generally less than 0.25.
Thoria	58–79 per cent.
Uranium Oxide	11.2–33.3 per cent.
Ferric Oxide	0.40–1.9 per cent.
Oxides of rare earths (Ce, La, Di, etc.)	1.00–6.9 per cent., but generally < 2 per cent.
Titania, Zirconia, and Alumina	Traces.

Concentration of Monazite Sand.—Saleable monazite sand is usually required to contain at least 3–4 per cent. **thoria,** and must therefore be concentrated so as to contain around 70 per cent. of monazite. This can be done by one of three general methods. In the **wet process,** monazite sand and a stream of water is run on to one corner of a rectangular concentrating table (such as the Wifley table shown in Fig. 1), which is tilted so that the material travels diagonally across it. By imparting a jigging motion to this table, the various minerals contained in the sand tend to arrange themselves roughly in order of their specific gravities. The method has, however, the disadvantage that small but heavy particles tend to behave in the same way as larger particles of lower specific gravity, and an efficient separation (*i.e.*, separation without substantial loss of monazite as "tailings") is therefore rather difficult. It has consequently been found expedient to confine the wet process to **initial** concentration, and to effect final separation of a marketable fraction by means of an **electro-magnetic process.**

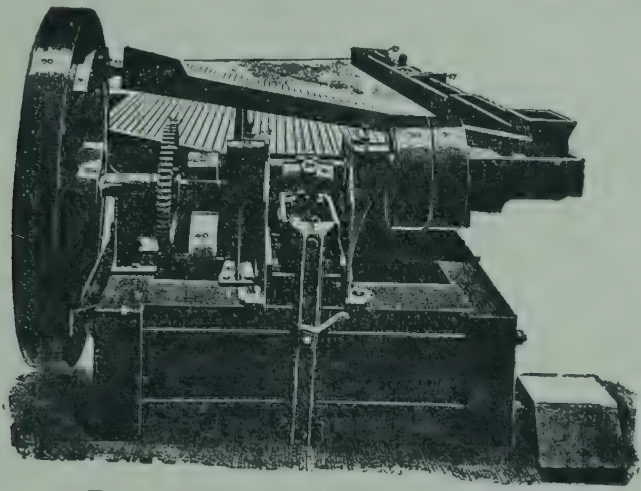


FIG. 1.—Movement End of Wifley Table.

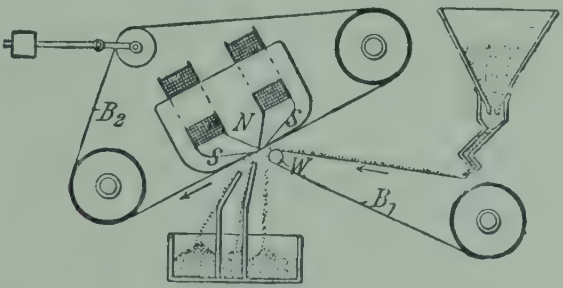


FIG. 2.—Wetherill Separator (Diagrammatic).

This is based on the fact that many minerals differ considerably in their magnetic permeability and that they will consequently suffer varying degrees of deflection in a strong magnetic field. A typical electro-magnetic unit, the Wetherill separator, is shown in Fig. 2: the thoroughly-dried sand is fed from a hopper on to the belt B_1, carried forward and thrown against the belt B_2 which travels just below the poles of the electro-magnet S, S. The separated fractions are then collected in the divider boxes, and by re-cycling the enriched monazite fraction it is normally possible to obtain 90–95 per cent. monazite in two or three runs.

The third concentration method, **dry blowing,** is less efficient than the electro-magnetic separation, but considerably cheaper, and has been successfully used in

Travancore. The principle is here the same as that underlying the wet process (*i.e.*, gravity separation), but instead of a jigging table, a shallow box enabling vertical segregation of the component minerals under the influence of an air-blast is used. A typical dry concentrator—the Sutton Steele table—is shown in Fig. 3. Air from a suction blower enters the table from below through a series of pipes and passes through a pervious top cloth to form an air film on the upper surface. This film causes the minerals to arrange themselves vertically in order of their specific gravities, and if a reciprocating motion is now imparted to the table, it is possible to separate them into fairly well-defined zones.

More recently, attempts have also been made to separate monazite by float-and-sink methods and by froth flotation processes. For a description of these reference should be made to any modern work on Ore Dressing.

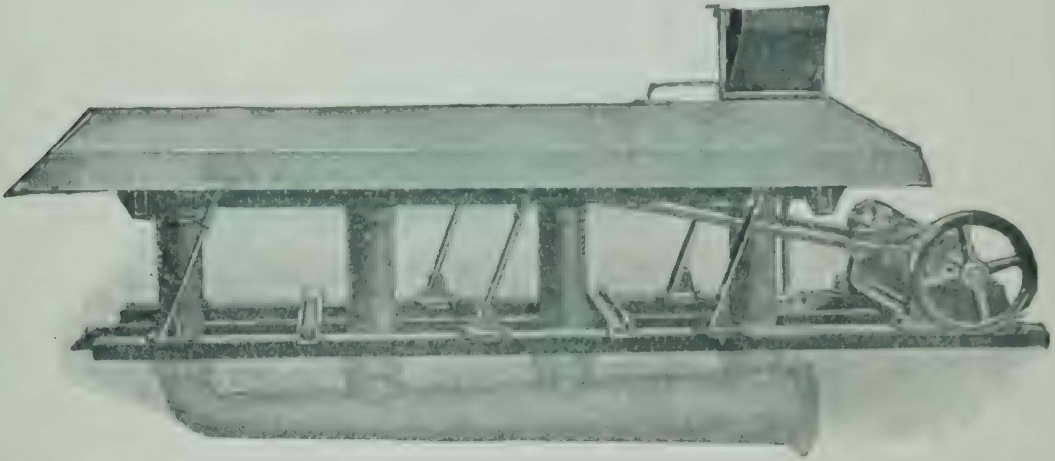


FIG. 3.—Sutton-Steele Dry Concentrating Table.

Extraction of Thorium. *A.* **The Purification of Thoria.**—Thorium in monazite is always associated with members of the cerium and yttrium group metals (which have similar chemical properties), and effective separation of these is difficult. Although several satisfactory *analytical* procedures are known, these are, without exception, far too expensive to be used in industry, and recourse is therefore made of a two-stage process which involves (i) "breaking" of concentrated monazite with strong sulphuric acid, and (ii) fractional crystallisation of the sulphates *or* fractional separation of the oxalates or double alkali carbonates.

In order to "break" the monazite, the concentrated mineral is heated in cast-iron pans with twice its own weight of strong sulphuric acid (sp. gr. 1.84) until the white pasty mass of sulphates, which results from this treatment, is completely soluble in water and no grains of yellow monazite remain. This operation is greatly facilitated by slowly adding the powdered mineral to *hot* acid. The sulphate mixture is then run into lead-lined vats and stirred with cold water until solution is complete. After allowing to stand for some time in order to permit insoluble matter (consisting mainly of silica, zircon, and rutile) to settle out, the solution of rare earth phosphates (in dilute H_2SO_4) is syphoned off and gradually neutralised with an alkali or alkaline earth, or greatly diluted with water. Since thorium is more basic than the other rare earths present in the solution, it is preferentially precipitated and can then be filtered off without difficulty. Care must, however, be taken to ensure that no thorium phosphate is lost in the waste filtrates, and in order to obtain a tolerably pure product it is also usually necessary to repeat the fractional precipitation by re-dissolving the thorium phosphate obtained from the first cycle in a minimum quantity of sulphuric acid and again diluting the solution with water. The proportion of thoria to other rare earth oxides in the final precipitate is normally of the order of 4 to 1.

The removal of **phosphoric acid** from the thorium precipitate is mostly kept secret, but a process developed by C. Baskerville, which effects the removal by volatilisation, may be of interest here. In this process, a mix consisting of 1 part of thorium phosphate, 1.1 parts of petroleum coke, 0.8 part of lime, and 0.15 part of fluorspar is heated for 1.5 hours in an electric furnace with a current of 35 volts and 125 amperes. When evolution of phosphorus ceases, the mass is cooled and treated with water in order to remove calcium hydroxide, and finally dissolved in hydrochloric acid. Owing to the presence of calcium carbide in the original mass, the solid will readily disintegrate when treated with water, and it is claimed that this eliminates several difficulties attaching to older processes. For example, according to German Patent 129,416 (1901) phosphoric acid can be removed by fusing the thorium precipitate with carbon and subsequently decomposing the resultant phosphides and carbides with hydrochloric acid. The fused mass is, however, extremely hard and difficult to grind, and complete decomposition is therefore difficult.

TABLE III

SOLUBILITIES OF THORIUM AND OTHER RARE EARTH SULPHATES

Sulphate.	14°–18° C.	25°–30° C.	42°–50° C.	50°–57° C.
$Th(SO_4)_2 + 8H_2O$	1.38 (15° C.)	1.85 (25° C.)	3.71 (44° C.)	1.94 (55° C.)*
$Ce_2(SO_4)_3 + 8H_2O$	11.06 (15° C.)	8.39 (25° C.)	5.65 (42° C.)	2.34 (57° C.)†
$Nd_2(SO_4)_3 + 8H_2O$	7.10 (16° C.)	5.10 (30° C.)	3.60 (50° C.)	...
$Pr_2(SO_4)_3 + 8H_2O$	14.05 (18° C.)	10.40 (25° C.)	...	7.02 (55° C.)
$La_2(SO_4)_3 + 8H_2O$	2.60 (14° C.)	1.90 (30° C.)	1.60 (50° C.)	...

* $Th(SO_4)_2 + 4H_2O$. † $Ce_2(SO_4)_3 + 4H_2O$.

The second step, *i.e.*, removal of associated rare earths other than thorium, is carried out by (i) fractional crystallisation of the sulphates, (ii) separation by means of the double alkali carbonates, or (iii) separation by means of the differential solubility of the oxalates.

The **sulphate method** is based upon the fact that thorium will form hydrated sulphates which, at certain temperatures, are considerably less soluble in water than the corresponding cerium earth sulphates. Thus, anhydrous thorium sulphate (prepared by the action of concentrated H_2SO_4 on thorium hydroxide at 400° C.) is soluble in ice-cold water to the extent of about 25 per cent. If the temperature of this solution is now raised up to about 45° C., the octahydrate $Th(SO_4)_2 + 8H_2O$ will separate, and if the temperature is raised still further, the tetrahydrate $Th(SO_4)_2 + 4H_2O$ is obtained. The solubilities of these sulphates in water are shown in Table III, together with the solubilities of the cerium earth sulphates. The figures represent in each case the quantity of sulphate (calculated as anhydrous) which can be dissolved in 100 gm. of water.

A consideration of these data shows at once that separation is most conveniently effected at between 15° C. and 20° C. At this temperature the octahydrate is obtained, and since this is precipitated in the form of dense crystals, the subsequent filtration and washing present no difficulty.

The **carbonate** method depends upon the fact that thorium carbonate forms soluble double salts with alkali carbonates, whilst the double carbonates of cerium earth metals are only very slightly soluble in water. For example, according to Hehner, 3.375 gm. of sodium carbonate can keep in solution 0.890 gm. of thoria but only 0.002 gm of ceria. From the separated thorium-alkali carbonate, thorium can then be recovered as oxalate (by addition of oxalic acid to the solution) or as hydroxide (by addition of caustic soda).

The **oxalate** method is based upon the ability of thorium oxalate to form soluble double salts with ammonium oxalate whilst cerium earth oxalates are virtually insoluble in solutions of this salt. Table IV shows the *relative* solubilities of rare earth oxalates (calculated as oxides) in excess ammonium oxalate.

In connection with these separation processes, however, attention must be drawn to the fact that their efficiencies are not as great as would appear from the solubility tables. The relative solubilities of thorium and cerium earth metals are not exactly maintained when these occur *together* in any one solution, and, in general, only about 85–90 per cent. of the thorium present in the source material is recovered. There is, on the other hand, a tendency for the efficiency of recovery to increase with the *scale* on which extraction operations are carried out.

Probably for these reasons, a set of separation processes based on the use of organic compounds has been discussed from time to time. For example, Kreidl and Heller have used ethylsulphate; C. R. Boehm converted thorium hydroxide into practically insoluble thorium acetate; and Garelli and Barbieri have used salicylic acid. Aniline, *m*-nitrobenzoic acid, sebacic acid, and fumaric acid have also been proposed, and Marden and his collaborators found that thorium could be electro-deposited from a mixed solution to which hydrofluoboric acid and lead hydroxide (or carbonate) had been added.

TABLE IV

RELATIVE SOLUBILITIES OF RARE EARTH OXALATES IN WATER
(Quantities calculated as Oxides)

Thorium - - - - -	2663.0	Neodymium - - - - -	1.5
Ytterbium - - - - -	105.0	Praseodymium - - - -	1.2
Yttrium - - - - -	11.0	Lanthanum - - - - -	1.0
Cerium - - - - -	1.8		

It might also be noted that a small but important source of thoria is found in waste mantle ash which is obtained from factory trimmings and used incandescent gas mantles. A typical extraction process here involves sieving the crude ash in order to remove as completely as possible the asbestos fibre used for attaching the mantle to its support, and treating the sieved ash with twice its weight of hot concentrated sulphuric acid for some hours. The paste obtained in this way is then poured into cold water, the rare earths precipitated by the addition of ammonium oxalate, and thorium separated from the precipitate by any of the methods described above.

Extraction of Thorium. *B.* Preparation of Metallic Thorium.—Possibly because of limited demand for metallic thorium, no single satisfactory method for its preparation has yet been worked out. Present methods generally involve electrolysis, but the product invariably contains appreciable proportions of thoria and requires further treatment. For example, electrolysis of a mixture of thorium chloride and sodium or potassium chloride in a graphite crucible at 800° C. gave a 40 per cent. recovery and a product containing 88.2 per cent. thorium, 11.6 per cent. thoria, 0.04 per cent. sodium, 0.03 per cent. silicon, 0.06 per cent. iron, and 0.15 per cent. carbon. A similar oxide content is found in products obtained by electrolysing potassium thorium chloride in a covered porcelain crucible at 600° C. with graphite electrodes in an oxygen free atmosphere. Somewhat better results are claimed for the use of rubidium thorium chloride, but no details are available and the process is probably uneconomic.

According to Siemens and Halske it is, however, possible to remove thoria from the impure metal by alloying with tin, lead, cadmium, copper, or aluminium, or by heating it with tantalum. In the latter case, it has been demonstrated that the resultant tantalum pentoxide can be removed by volatilisation.

Other methods of preparing metallic thorium include—

(i) reduction of thoria with hydrogen at high temperatures and a pressure of 5 atmospheres (H. von Wartenberg),
(ii) decomposition of thorium halides at high temperatures in the presence of reducing agents such as carbon (Siebert and Korten), and
(iii) thermal decomposition of thorium tetrahalides on a heated tungsten filament (van Arkel and de Boer).

This last method is similar to that occasionally employed for the preparation of metallic titanium.

It is also of interest to note that whilst alkali metals have little or no effect on thoria even at high temperatures, reduction of thoria with calcium yields about 62 per cent. of the metal (Ruff and Brintzinger).

Analysis of Thorium Minerals.—The complete analysis of a thorium mineral is usually a long and tedious operation requiring much experience if accurate results are to be obtained, and the necessary operations are too complicated to be described here in detail.

A method for the complete analysis of monazite sand, which permits of the whole operation being carried out on one portion of the sample, has been described by Johnstone (*Journ. Soc. Chem. Ind.*, **33**, 56, 1914), and is briefly as follows:—

The finely ground mineral is digested with hot concentrated sulphuric acid until all the monazite has been decomposed, and the pasty mass of sulphates is then treated with cold water. After separation of the insoluble silica, by filtration, the rare earths in the acid solution are precipitated by means of ammonium oxalate. Thorium is estimated in this precipitate by the thiosulphate method (see standard method given below). The cerium, lanthanum, and yttrium earths in the thiosulphate filtrate are recovered by treating the solution with concentrated nitric acid, and then precipitating them by means of ammonia. Yttrium is separated from the cerium and lanthanum in this precipitate by fractional crystallisation of the double potassium sulphates, the yttrium salt remaining in solution. Cerium is separated from the lanthanum and didymium earths by converting all to hydroxides and treating with a current of chlorine whilst suspended in a fairly strong solution of caustic potash. This treatment causes the lanthanum and didymium earths to pass into solution, whilst the cerium is converted into the insoluble hydrated peroxide. The filtrates from the precipitation with ammonium oxalate contain the iron, aluminium, calcium, and phosphoric acid, and after destroying the oxalate, by evaporation to dryness with nitric acid, these constituents are estimated by the ordinary methods of analysis. The accurate quantitative estimation of thorium in monazite is now a matter of considerable technical importance, and the following detailed account by E. White ("Thorium and Its Compounds"), of a variation of the thiosulphate method, may be quoted, as it is stated to be the standard process employed commercially.

Standard Method.—12.5 g. of sand are heated to 180°–200° C. for two or three hours, or until all monazite grains are "broken," with 50 c.c. H_2SO_4. (Examine a small portion mixed with water on a watch glass.) The white pasty mass is cooled and dissolved in water sufficient to produce 500 c.c. of solution when cold. Filter when cold and take 200 c.c. of the solution (equal to 5 g. of sample), dilute with water to 500 c.c., and add, without stirring, 180 c.c. of a cold saturated solution of oxalic acid, and allow to stand until the bulky flocculent precipitate becomes heavy and crystalline (half to one hour as a rule); stir and set aside for twelve hours or overnight. Filter, reject filtrate, wash the precipitate until the washings give no reaction for phosphate with ammonium molybdate solution. (If necessary, use water acidulated with hydrochloric acid for washing.) Dry and ignite the oxalates and filter paper. Dissolve the oxides in hydrochloric acid (sp. gr. 1.16), rinsing the crucible with alcohol, if necessary. Evaporate the hydrochloric solution to dryness on a water-bath, take up with a few c.c. of water, and again evaporate to dryness. Dissolve the acid free chlorides in 250 c.c. water, and add 9 g. of $Na_2S_2O_3 + 5$ Aq. in 30 c.c. water; set aside overnight, boil for ten minutes, filter and wash the precipitate until the washings give no reaction with ammonia. Keep both precipitate and filtrate. The filtrate is again boiled for sixty minutes, and any further precipitate formed is collected, washed, kept aside, and marked "A," the filtrate being then rejected. The precipitate produced by the ten minutes' boiling is dissolved on the filter with 5 per cent. hydrochloric acid by passing the acid several times through the filter, which is then washed with boiling water. The acid solution is evaporated to dryness on a water-bath, taken up with 150 c.c. of water, and precipitated with 3 g. of sodium thiosulphate in 10 c.c. of water, set aside overnight, boiled ten minutes and filtered, and the filter washed with water. The filtrate is boiled after adding ammonia in excess, and the precipitated hydroxides are collected and set aside with precipitate "A" to rework. The thiosulphate precipitate is dissolved in 5 per cent. hydrochloric acid, as before, evaporated, taken up, and reprecipitated with sodium thiosulphate solution, set aside, boiled, filtered, and the filtrate tested with ammonia. If the filtrate gives any precipitate with ammonia, the thiosulphate treatment is repeated until the solution gives no precipitate with ammonia. Three thiosulphate precipitations in all are generally sufficient. The final thiosulphate precipitate is dissolved on the filter in 5 per cent. hydrochloric acid, the filter washed with boiling water, and the filtrate made up to 150 c.c.; 10 c.c. hydrochloric acid are added, and then 30 c.c. of cold saturated solution of oxalic acid. The whole is kept at 30°–40° C. for two or three hours, and then set aside overnight, filtered, and the precipitate washed, dried, and ignited. The filter papers from the thiosulphate precipitates, the precipitate "A," and all subsequent ammonia precipitates are reworked for traces of thorium which they may contain. They generally yield about 5 mg. of ThO_2, equal to 0.1 per cent. on the 5 g. taken.

Physical Properties of Thorium.—Thorium is a greyish-white metal resembling nickel but belonging to the titanium group of metals. Its specific gravity is 11.3; its melting point (when pure) lies around 1,700° C.; and its boiling point has been estimated as of the order of 3,090° C. Lower values periodically reported in the literature are almost certainly due to impurities in the metal under test.

The electrical and heat conductivities with respect to Silver = 100 have both been given as 9.0, and the specific heat between 0° and 100° C. as 0.2757 (L. F. Nilson). The coefficient of linear expansion ($a \times 10^6$) over the range 0°–100° C. is 12.1 (Marden *et al.*), but will be rather lower if the metal is prepared by reduction of thoria with calcium.

According to Moissan and Etard, the metal is sufficiently hard to scratch glass.

Among the **chemical** properties of thorium, the complete stability towards water and aqueous solutions of alkalies may be noted. According to Nilson *et al.*, thorium is also stable in air or oxygen at ordinary, or moderate, temperatures, but will oxidise with increasing rapidity when heated in air at temperatures above about 120° C. Ignition occurs when it is heated in air to dull redness.

Of the common mineral acids, only sulphuric acid appears to have an appreciable effect on the metal, but even with this only a slow reaction will normally occur. A rapid reaction between thorium and nitric acid has been claimed by J. J. Chydenius, but this claim has not been substantiated, and it is probable that Chydenius' observation rested upon the use of *impure* thorium.

It is also of interest that thorium is capable of reducing many metals and metalloids from their compounds.

For a discussion of the **radioactivity** of thorium see Volume VII of Mellor's "Treatise on Inorganic and Theoretical Chemistry," and Table I of Section LXXXV, "Radioactive Substances."

Industrial Utilisation of Thorium.—At present, **metallic** thorium finds only very limited application in industry. Small quantities are, for example, employed in certain X-ray and glow-discharge lamps; the photo-electric properties of thorium are used in measuring restricted portions of the ultra-violet spectrum; and an alloy of thorium and tungsten has been recommended by Siemens and Halske for the manufacture of filaments for incandescent lamps. It is, however, possible that the metal may become important as the result of current research work in the field of Nuclear Power (see Section XC). In the meantime, the bulk of the world's thorium output finds use as **thoria** in the **incandescent mantle industry.**

THE INCANDESCENT MANTLE INDUSTRY

This industry may be said to have started in 1884, when Auer von Welsbach patented the use of a fibrous network of rare earth oxides as a lighting medium. Early mantles made of zirconia and the oxides of lanthanum and yttrium were, however, not very successful (mainly because of their intrinsic weakness), and, in 1893, Welsbach accordingly patented the use of a mixture containing 98–99 per cent. thoria and 1–2 per cent. ceria. It was shown that this mixture possessed maximum luminosity; pure thoria emits only relatively little light, and the luminosity is also decreased progressively if the ceria content is increased beyond about 2 per cent. A curve showing the dependence of luminosity upon the ceria content of a thoria-ceria mixture is shown in Fig. 4; the data used for its construction have been reported by Drossbach (*J. fuer Gasbel.*, **41**, 352, 1898) and Lux (*Zeits. fuer Beleuchtung*, 246, 1907).

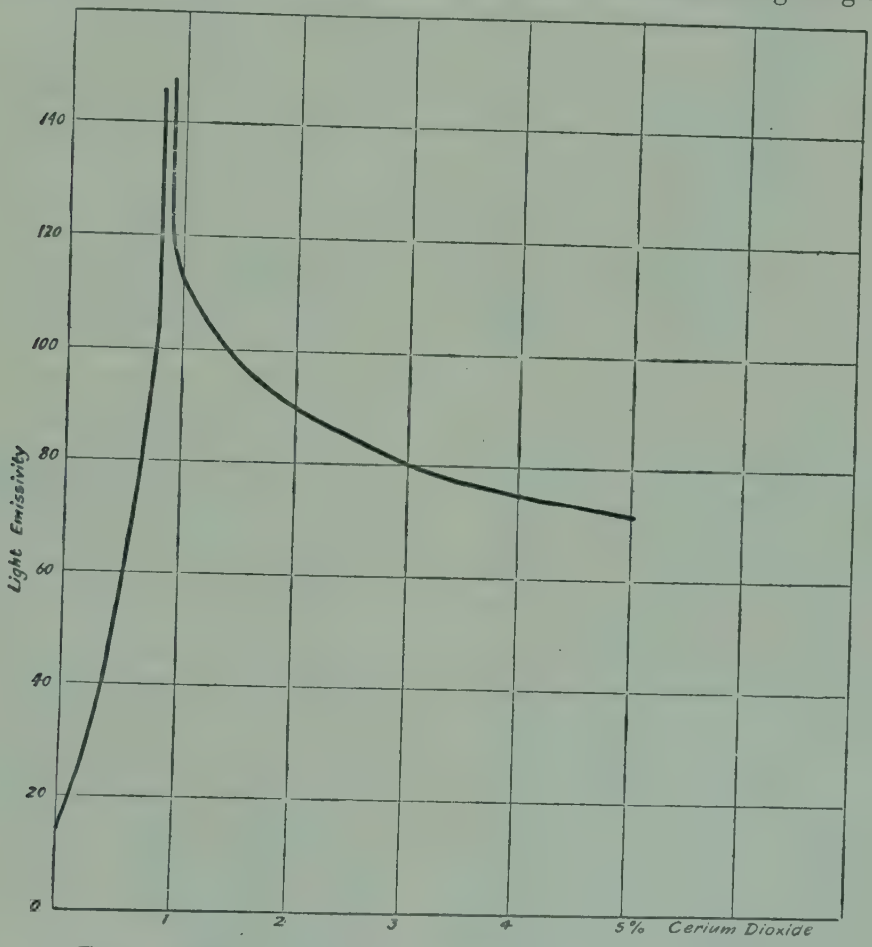


FIG. 4.—Effect of Cerium Dioxide on the emissivity of Thoria.

The present method of manufacture of gas mantles is somewhat as follows:—

(*a*) **Fabric.**—Early mantles were made of cotton, but as these were found to give a decreased luminosity after being in use for a short time, this material has now been almost completely supplanted by **ramie** fibre or **artificial silk**. The latter combines the illuminating power of ramie with a high elasticity of the ash skeleton and has consequently been claimed to be superior to ramie. It may be pointed out that silk mantles have the further advantage that they do not require washing before impregnation. The appearance of the impregnated fibres made from cotton, ramie, and artificial silk before and after "burning off" are shown in Figs. 5–8.

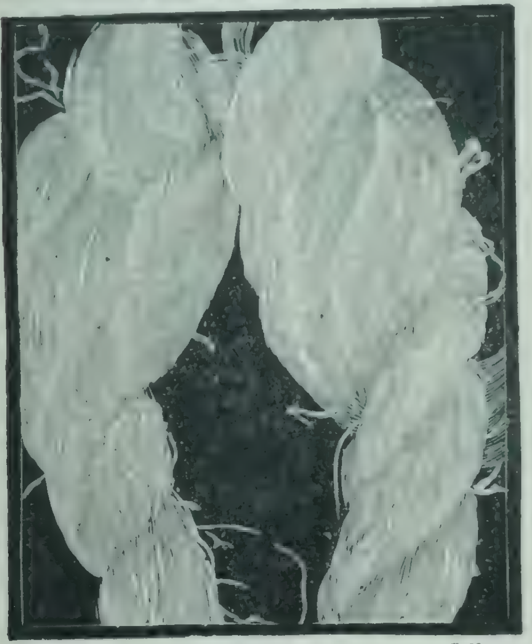


FIG. 5.—Cotton before Burning Off.

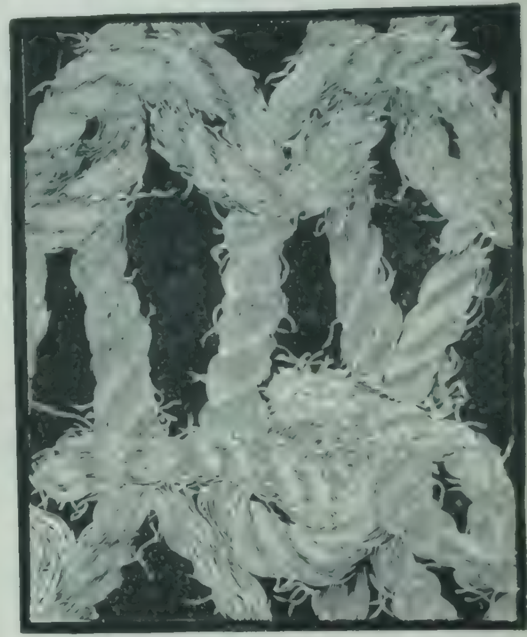


FIG. 6.—Cotton after Burning Off.

(*Reproduced by permission from Thorpe's "Dictionary of Applied Chemistry."*)

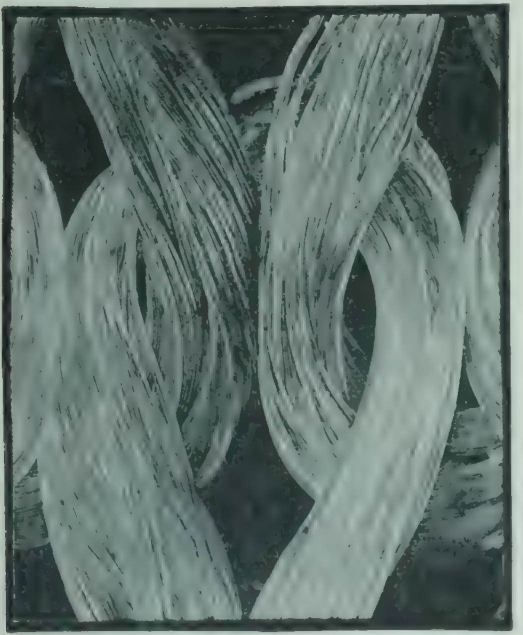


FIG. 7.—Collodion before Burning Off.

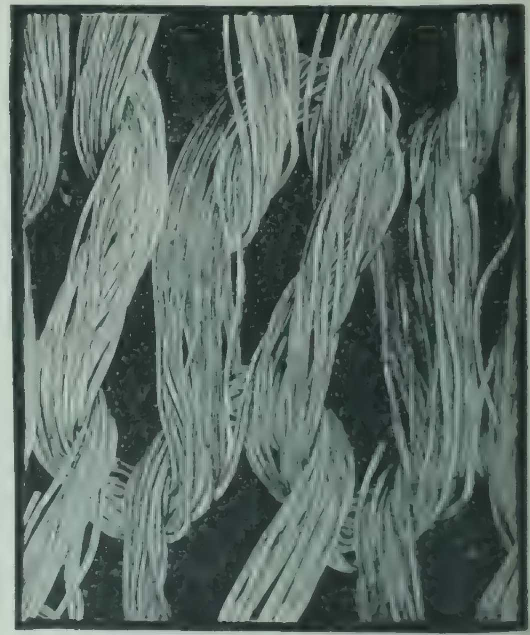


FIG. 8.—Collodion after Burning Off.

(*Reproduced by permission from Thorpe's "Dictionary of Applied Chemistry."*)

(*b*) **Washing.**—Before being impregnated with the solution of the rare earths (see below), the knitted fabric (or "stocking") must be washed in order to remove fatty matter and reduce the proportion of inorganic material. In the case of ramie fabric, this is done by soaking the mantle in dilute (2 per cent.) nitric acid for 12–15 hours, washing it with distilled water, treating it with dilute ammonia, and finally rinsing it thoroughly with water. Cotton mantles are washed in a warm 3–5 per cent. solution of caustic soda and finally in 1–3 per cent. aqueous hydrochloric acid solution.

The ash content of the mantles after washing is normally of the order of 0.02 per cent., and consists largely of iron oxide and silica. A reduction of the ash to below 0.01 per cent. is stated to be detrimental to the strength of the ash skeleton.

(*c*) **Drying.**—This is usually done by centrifuging the mantles and finally drying in a current of hot air.

(*d*) **Impregnation.**—For this purpose, a solution containing between 25 and 50 per cent. of thorium and cerium **nitrates** (in the ratio of 99 : 1) is used, and small quantities of beryllium or magnesium nitrate are frequently added in order to confer greater strength upon the ash skeleton. A typical impregnating solution has the following composition: thorium nitrate 1,000 gm., cerium nitrate 10 gm., beryllium nitrate 2–5 gm., magnesium nitrate 1.5–2.5 gm., distilled water 1,600–2,400 gm. (The proportion of water depends upon whether the mantles are intended for use with low or high pressure gas.) The time of impregnation varies from about two minutes (in the case of cotton or ramie mantles) to 5 hours (in the case of artificial silk mantles). After impregnation, superfluous liquid is removed by passing the mantles through a roller (in the case of cotton or ramie) or by centrifuging (in the case of silk), and finally by drying at about 30° C. With cotton and ramie, this last step is carried out after cutting the mantles into lengths and stretching them on glass drying cylinders; silk mantles are usually dried in lengths on wooden rollers and cut *after* drying.

(*e*) **Fixing.**—After drying and cutting, upright mantles are fitted with a sewn-on tulle head and asbestos loop, and inverted mantles drawn together to form the "spider," and fixed to a supporting ring. Head, loop, and ring are then strengthened by treating them with a thorium nitrate solution containing considerable proportions of calcium, aluminium, or magnesium salts; on burning off, the portions of the mantle so treated shrink more than the body and become correspondingly more compact.

A suitable machine for strengthening mantles is shown in Fig. 9. In this, a felt pad saturated with the fixing solution is pressed against the dried impregnated mantle whilst this is slowly rotated. A small quantity of methylene blue is often added to the solution in order to show where it has been applied.

(*f*) **Branding.**—If it is desired to brand the mantle with a trade mark, etc., the design is stamped on with a solution containing—

Didymium nitrate - - - - -	1,000 gm.
Glycerine - - - - - -	200 ,,
Methylene blue - - - - -	25 ,,
Alcohol (96 per cent.) - - - -	300 ,,
Distilled water - - - - -	500 ,,

This solution gives a brand that is easily visible both before and after burning off.

(*g*) **Burning Off.**—After final shaping on a wooden model, the mantle is burnt off *from the top* with a Bunsen flame. This operation was formerly performed by hand, but is now generally carried out by a machine such as that illustrated in Fig. 10. This consists essentially of two rows of gas burners mounted on an adjustable frame and of a removable bar provided with clips for the mantles. Provision is also made for controlling the gas pressure.

Burning off is usually started with low gas pressure until the mantles are fully carbonised, and completed with high gas pressure. The process takes from about 1.5–15 minutes, according to the size of the mantle.

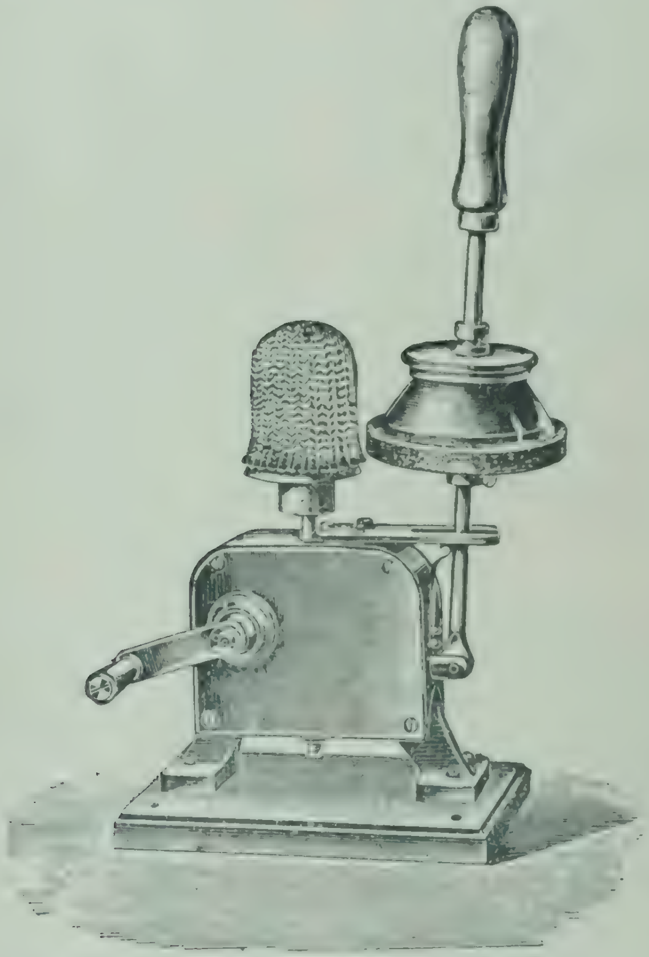


FIG. 9.—Machine for Applying "Fixing" Solution to Inverted Mantles, ⅙ Actual Size.

(*h*) **Collodionising.**—In order to strengthen the burnt-off mantles, it is customary to collodionise them by immersion in a solution containing about 100 parts of a 4 per cent. collodion solution, 40 parts of ether, 6.5 parts of camphor, and 3.5 parts of caster oil. Some manufacturers also add inorganic salts, such as the nitrates of thorium, beryllium, zirconium, to the collodionising solution.

On a small scale, collodionising is done by suspending the mantles on a metal frame and lowering the whole into the bath. On a large scale, it is customary to use closed collodionising chambers in which provision is made for condensation (and collection) of the volatile vapours evolved.

Finally, the mantles are dried at 50°–60° C. and trimmed.

It is to be noted, however, that burning off must, in the case of mantles made from artificial silk other than viscose silk, be preceded by "de-nitration." This can be done by immersing the impregnated fabric in alcohol (95 per cent.) to which a little hydrofluoric acid has been added. The thorium is then precipitated in an insoluble and viscous form, and the fabric can then be worked as is ramie or cotton. A useful review of the use of artificial silk for the manufacture of incandescent mantles has been given by Wirth (*Chem. Zeit.*, 35, 752, 1911).

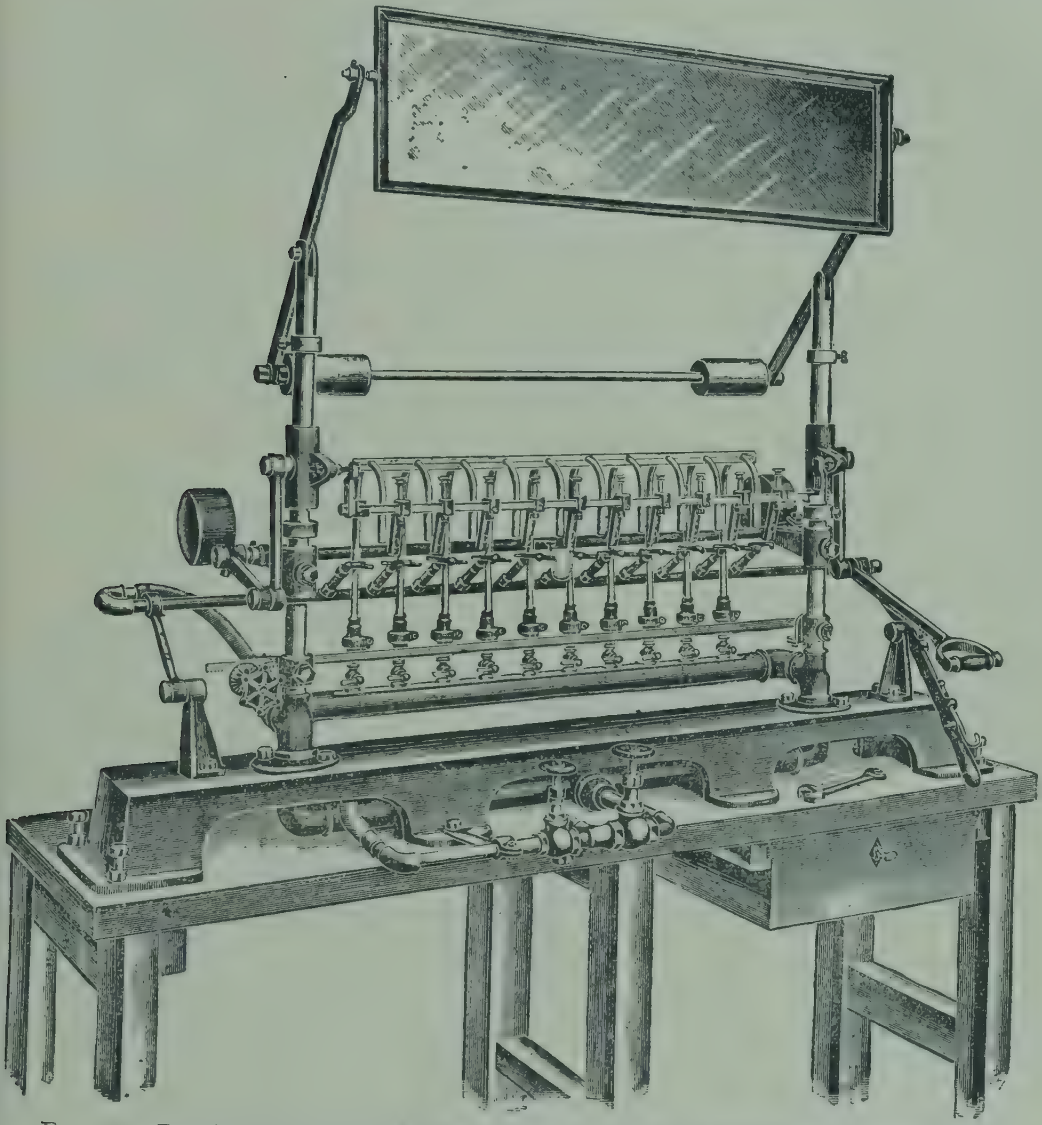


FIG. 10.—Burning Off and Hardening Machine for Inverted Mantles, $\frac{1}{14}$ Actual Size.

Testing of Thorium Nitrate for Mantle Manufacture

The following is a brief summary of the tests which thorium nitrate is usually required to pass in order to satisfy the requirements of mantle manufacturers:—

Solubility and Colour.—When 25 g. of the nitrate is stirred with 25 c.c. of distilled water, for ten minutes, it should be completely soluble, and the solution should have only a slight yellow colour.

Ignition.—The nitrate, after ignition in a platinum crucible for thirty minutes in a blast flame, should leave a residue of not less than 48 per cent. The ash should be quite white and free from any pink or yellow tint.

Cerium.—Dissolve 2 g. in 10 c.c. of distilled water, and add sufficient potassium carbonate solution to dissolve the precipitate first formed. The addition of a few drops of hydrogen peroxide to this solution should not give any appreciable colour. This test will indicate 0.004 g. of cerium oxide.

Didymium.—The ash produced by the above ignition is suspended by a platinum wire for two minutes in the flame of a Bunsen burner. After cooling and crushing, the ash will be pink if didymium oxide is present. This test is very sensitive. The yellow colour imparted to the flame in this test should be only transient, and the ash should show practically no luminosity in the ordinary (not blast) Bunsen flame. The presence of almost any inorganic impurity will cause the ash to become luminous.

Iron and the Heavy Metals.—Only a slight coloration should be produced on mixing a 30 per cent. solution of the nitrate with an equal volume of a 2 per cent. solution of ammonium thiocyanate. To test for the heavy metals, 20 c.c. of a 30 per cent. solution is mixed with 50 c.c. of water saturated with sulphuretted hydrogen. At the most, only a slight darkening should be produced without any trace of a permanent precipitate.

Phosphoric Acid.—The nitrate should not contain more than 0.004 per cent. of P_2O_5. For the quantitative determination of this constituent about 25 g. of the sample is taken, and the phosphate is precipitated in the usual way with ammonium molybdate in acid solution.

Sulphuric Acid.—The determination of sulphate in the presence of thorium nitrate by the usual method of precipitation with barium chloride gives low results. E. White recommends fusing the nitrate with four times its weight of solid potassium hydroxide, extracting the mass with water, and after filtering off the insoluble matter, determining the sulphate in the filtrate in the usual manner. An alternative process is to dissolve 10 g. of the nitrate in 250 c.c. of distilled water and to add 5 c.c. of hydrochloric acid and 5 g. of oxalic acid. After allowing to stand for some hours, an aliquot part of the clear liquid is filtered off and the sulphate estimated in the usual manner.

Makers of mantles usually require a nitrate which, on ignition, shall leave a soft voluminous ash, and for this purpose sulphuric acid is added to the nitrate before crystallisation, so that the finished nitrate contains about 2 per cent. of sulphate. Thorium nitrate free from sulphate leaves, on ignition, a hard dense ash unsuitable for mantle manufacture by the ordinary process.

Aluminium, Calcium, Magnesium, and Sodium, together with the iron and phosphoric acid, are determined by precipitating the rare earths with oxalic acid, evaporating the filtrate to dryness, and weighing the residue remaining after ignition, which should not amount to more than 0.05 per cent. of the original thorium nitrate.

Influence of Impurities.—Alkalis and alkaline earths in the body of the mantles cause them to shrink and lose their shape. Phosphates cause excessive brittleness, whilst didymium and lanthanum produce a decrease in luminosity. Traces of iron and the heavy metals have but little effect, as they are largely volatilised during the ignition of the mantle.

Occurrence of Radioactive Thorium Minerals.—The above table shows the composition, occurrence, structure, appearance, and some physical properties of thorium containing minerals, based on the "Abridged Table of Uranium and Thorium Minerals," by Nucleonic and Radiological Developments Ltd. Other radioactive minerals containing smaller proportions of thorium are given in related tables in the section on Uranium.

TABLE I.—OCCURRENCE OF RADIOACTIVE THORIUM ORES

Name and Composition.	Occurrence.	Known deposits.	Structure.	Colour, Lustre.	S.G.	H.	%	Remarks.
ALLANITE (P). Hydrous aluminium, silicate of rare earths, iron and calcium.	Pegmatites, granites, syenites, gneisses.	U.S.A., Urals, Norway, Saxony, Sweden, Canada, Greenland, Madagascar.	Monoclinic (long slender).	Brownish, resinous.	3·5 to 4	5·5 to 6		= ORTHITE. Contains small and variable percentage of U. and Th.
AMPANGABEITE. Hydrated niobate and titanate of uranium, thorium, iron and other minor constituents.	(Pegmatite with columbite).	Madagascar.	Orthorhombic.	Brownish red, greasy.	4	4	6	Also reported in Brazil.
BETAFITE (P). Hydrated titanoniobate of U. and Th., calcium, iron and other minor constituents.	Pegmatites.	Madagascar.	Isometric opaque.	Greenish black or dark brown, greasy.	4	5	25	Brittle with conchoidal fracture.
MACKINTOSHITE. Hydrous silicate of uranium, thorium, cerium, etc.		Western Australia, Texas.	Massive or tetragonal.	Black.	5·42	5·5	22 – 45 –	UO_2. ThO_2.
MAITLANDITE (S).	Pegmatites.	Western Australia.	Amorphous vitreous.	Black.			35·6 25·0	of uranium oxides. of thorium oxides.
MONAZITE (P). Phosphate of rare earths, with thorium and uranium.	Beach sands, pegmatites and granites.	Australia, India, Norway, Madagascar, U.S.S.R., France, South Africa, U.S.A., Canada, Brazil.	Monoclinic but usually found in irregular masses.	Yellow to brown, vitreous or resinous.	4·9 to 5·3	5·5	16	of thorium. Slightly magnetic and therefore susceptible to magnetic separation fracture uneven. Sub-transparent to sub-transluscent.
NICOLAYITE (S).			Amorphous sub-vitreous, brittle.	Yellow, resinous.			37·3 24·5	of uranium oxides. of thorium oxides.
PILBARITE (S).		Australia.	Massive.	Canary yellow, dull.			27 31·3	of uranium oxides. of thorium oxides.
THORIANITE (P). Thorium and uranium oxides. (Apparently isomorphous mixture.)	Alluvial gravels derived from pegmatites, igneous rocks.	Ceylon, Siberia, Madagascar.	Isometric crystals, usually cubic.	Black, horny.	9·5	6·5	30	Fracture uneven. Usually found as waterworn pebbles.
THORITE (P). Hydrated thorium silicate plus rare earths, uranium, etc.	Mainly in syenites, pegmatites, also with gold and tin alluvials.		Tetragonal cubic crystals or square prisms with pyramidal ends or massive form.	Black brown to orange yellow, vitreous or resinous.	4·5 to 5·4	4·3 to 5·0	3	Conchoidal fracture. Uranium content usually small.
URANOTHORITE. Variety of thorite.	Tin bearing sands, gold "placers" and gem gravels.	Nigeria, Norway, New Zealand, Canada, Ceylon.					17	Thorite but richer in uranium up to 17 per cent.

P = Primary; S = Secondary; H = Hardness (Moh's scale); % = Percentage thorium or uranium oxide.

PART II—CERIUM

LITERATURE

F. Peters.—"Seltene Erdelemente im Einzelnen." See Gmelin-Kraute.—"Handbuch der Anorganischen Chemie," Vol. VI, Pt. II.

R. B. Gordon.—"Rare Earths and Minor Metals." John Crerar Library, Chicago, Ref. List No. 48, 1941.

Smith Chemical Co., Inc.—"Cerium Sulphate." Columbus, Ohio, 1935.

Anon.—"Cerium Oxide boosts Enamel Reflectance." *Ceram. Ind.*, 53, 62 (1949).

B.I.O.S. 400.—"The Cerium Industry in German Territory, including Reports on Radium and Mesothorium."

F.I.A.T. 750.—"Rare and Minor Metals."

C. R. Boehm.—"Die Verwendung der Seltenen Erden." Leipzig, 1913.

CERIUM

Cerium (atomic weight = 140.125; atomic number 58) is by far the most common of the so-called "rare earth" elements, and probably occurs more frequently even than silver. It is chiefly found as the tetravalent oxide **ceria** (CeO_2), which forms the major constituent of **Cerite, Monazite, Orthite,** and **Gadolinite**; in Monazite, for example, ceria occurs to the extent of 25–35 per cent.

Natural Occurrence of Cerium Earths.—Cerium and cerium earths occur in more than fifty minerals, and it is therefore only possible here to mention the most important sources of Ce.

Cerite (also known as Ochorite or Cererite) is a hydrated silicate of cerium group metals, and contains as major components cerium, lanthanum, and didymium. Crystals (orthorhombic) are rare, and the mineral is normally found in the form of reddish amorphous masses. A major deposit of cerite is located near Bastnaes in Sweden.

Monazite (see "Thorium") is a yellow to dark reddish-brown orthophosphate of cerium earth metals, including cerium, lanthanum, praseodymium, and neodymium, and may also contain up to 18 per cent. of thorium.

Extensive deposits of monazite sand (of alluvial origin) occur on the sea-coast of Brazil (particularly near Bahia and Rio de Janeiro), in Carolina (U.S.A.), in Travancore (Malay States), and in Ceylon and Nigeria. Monazite also exists in several gneissic and granitic rocks, but its working from these deposits is now uneconomical and has been discontinued.

Orthite (also known as **Allanite**) is a double silicate of aluminium and cerium earth metals, but also contains smaller quantities of thorium, calcium, and yttrium earths. The mineral occurs in Sweden, Greenland, the United States, and the Ural mountains of Russia, and smaller deposits are found in Germany.

Secondary sources of cerium are the yttrium-bearing minerals **Gadolinite** and **Yttrialite.**

The cerium contents of the more important sources are shown below:

Monazite (Nigeria) - -	30.5–36.5	per cent.	cerium	earths	
Monazite (Ceylon) - -	20.6–27.5	,,	,,	,,	
Monazite (Malaya) - -	25.4–33.7	,,	,,	,,	
Cerite - - - -	up to 64.5	,,	,,	,,	
Orthite - - - -	15.0–25.0	,,	,,	,,	and related
Gadolinite - - - -	5.0–10.0	,,	,,	,,	

Cost of Cerium.—The price of cerium metal is about £7, 15s. 0d. per lb.; "mischmetall"—containing about 50 per cent. Ce, 40 per cent. cerium group metals, such as lanthanum, samarium, and neodymium, and 10 per cent. yttrium elements and iron—sells at about £1, 15s. 0d. per lb.

Separation of Ceria from Associated Oxides.—In order to free ceric oxide from associated oxides, such as lanthana, neodymia, yttria, and samaria (*i.e.*, oxides of the cerium *group* of metals), the following methods have been used successfully:—

1. The mixed hydroxides are suspended in a solution of potassium or sodium hydroxide, and treated with a stream of gaseous chlorine until the solution has been neutralised. Ceric hydroxide then remains in suspension whilst the other hydroxides are converted into soluble chlorides or hypochlorites (*cf.* P. Mengel, *Zeitschr. anorg. Chem.*, **19**, 67, 1899).

2. The mixed oxides are dissolved in hot nitric acid, and the solution evaporated to dryness with ammonium nitrate until ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ separates (*cf.* Welsbach, *Monatsh.*, **5**, 508, 1884; Schottlaender, *Ber.*, **25**, 378, 1892). The double nitrate, which forms bright red, hygroscopic crystals, can then be recrystallised from nitric acid, and ignited to form pure ceria.

3. The mixed nitrates, obtained by dissolving the oxides in hot nitric acid, are neutralised with ammonia and boiled with magnesium or sodium acetate and hydrogen peroxide. Cerium is thereby quantitatively converted into the insoluble basic acetate which can be ignited to ceria (*cf.* Meyer and Koss, *Ber.*, **35**, 672, 1902).

4. A common process consists in converting the mixed oxides into the nitrates, and treating a solution of these with potassium permanganate in the presence of a basic substance, such as sodium carbonate or the oxides of zinc, mercury, or magnesium (*cf.* Beyer, *Zeitschr. anorg. Chem.*, **37**, 378, 1903; Drossbach, *Ber.*, **29**, 2452, 1896; German Patent No. 143,106). This process yields a precipitate containing cerium in the form of the hydroxide.

Metallic Cerium.—Metallic cerium may be prepared by the electrolysis of fused cerous chloride, $CeCl_3$, with or without the addition of barium, calcium, or alkali chlorides, or by the electrolysis of a mixture of cerous fluoride, CeF_3, and ceria.

Very pure cerium metal is best obtained by electrolysing fused cerous chloride in a cell containing a carbon anode and molybdenum cathode (*cf.* Tombe, *Trans. Electrochem. Soc.*, **66**, 231, 1934).

The metal has the appearance of iron, and melts at approximately 630° C. It is relatively stable in air, but tarnishes due to the formation of a surface skin of yellow CeO_2. It is slightly attacked by cold water and will react moderately quickly with boiling water to evolve hydrogen and form the hydroxide. It is also readily soluble in acids, though *concentrated* nitric acid forms a deposit consisting mainly of ceria.

When filed the metal releases a shower of sparks that are sufficient to ignite an inflammable gas; this phenomenon is made use of in the pyrophoric alloys industry which is referred to below.

Alloys of cerium can be made by the simple expedient of melting the components under fused potassium and sodium chlorides (*cf.* Muthmann and Beck, *Ann.*, **331**, 46, 1904), but even under these conditions the combination may proceed violently. This applies particularly to the formation of a 1 : 2 Ce–Al alloy.

Despite this difficulty, however, a fair number of cerium-bearing alloys are manufactured on a large scale. Typical examples are provided by the "Ceralumin" series developed by J. Stone & Co., Deptford; the cerium content of these alloys varies between 0.05 and 2.0 per cent., and it is claimed that this addition performs the same function as a larger addition of titanium: it has a marked refining influence upon the microstructure of the alloy, and suppresses the formation of brittle iron-aluminium compounds.

More recently it has also been stated that the addition of a small quantity of cerium improves the mechanical properties of magnesium at high temperatures.

Cerium in Industry.—Apart from alloying, the most important application of cerium is found in the **pyrophoric alloys industry.** This industry dates back to about 1903, when Auer von Welsbach found that mixed cerium earth metals would, when filed, release sparks that were sufficient to ignite inflammable gases. This property was later (1909) traced to the presence of a superficial oxide layer that required frequent renewal, and numerous patents were accordingly taken out to cover production of the layer.

Since then, however, several important advances have been made. In particular, the need for renewal of the oxide layer was obviated by the discovery that alloys of cerium earth metals with certain heavy metals, such as iron, nickel, manganese, or cobalt, possessed *permanent* pyrophoric properties. This, for example, is the case with the "mischmetall" or "Auer metal," which contains about 35 per cent. of iron and 65 per cent. of cerium earths.

It is to be noted, however, that the production of "mischmetall" is attended by difficulties which arise from the extreme reactivity of the alloy: "mischmetall" will, for example, combine readily with oxygen, nitrogen, and hydrogen, and will even remove oxygen from carbon monoxide and dioxide. The reduction of the mixed oxides to the metallic state must therefore be carried out *in vacuo*. Similar precautions must be taken if the pyrophoric alloy is produced from the mixed chlorides by electrolysis; a typical process is then as follows:—

Stage 1.—The mixed chlorides are carefully dehydrated in order to obtain a product with the highest possible equivalent oxide content. With calcium chloride, this equivalent cannot normally be carried to beyond about 40–50 per cent., and if a higher grade product is required, it is necessary to heat the mixed chlorides with ammonium chloride until the latter is completely volatilised. This process is economically unsound unless the ammonium chloride can be recovered. An alternative, described in German Patent 172,529 (1912) by Borchers and Stockem, is therefore as follows: A mixture of anhydrous cerium earth chlorides and oxychlorides, obtained by heating the hydrated chlorides to a high temperature, is treated with alcohol, the solution separated from the insoluble oxychloride residue, and the anhydrous chlorides recovered by evaporation of the alcoholic solution. Organic matter can be removed by heating the anhydrous residue in a current of dry air to moderate temperatures.

Stage 2.—The dry chlorides are electrolysed in a graphite crucible containing a large iron cathode. In order to do this on a remunerative scale, however, it is necessary to have a cheap source of electric power, and to work with not less than about 1,500 amperes.

Apart from the ferro-alloys, several pyrophoric alloys containing "mischmetall" and **silicon, boron,** or **titanium** have also been patented (*cf.* British Patent 27,341 and French Patent 396,198); it is claimed that these alloys are as efficient as the ferro-alloys, but that they can be produced more cheaply by simply melting the metals in a magnesia crucible under sodium chloride. (It might be noted here that a still cheaper pyrophoric alloy is said to be a mixture consisting of manganese and antimony with as little as 5 per cent. "mischmetall.")

Finally, attention may be drawn to pyrophoric alloys consisting of cerium earth metals with **cadmium, zinc, tin,** or **lead** (*cf.* U.S.A. Patent 1,102,575) and of "mischmetall" and **mercury** (*cf.* British Patent 15,507). The latter do not, however, appear to have been put to any major technical use, even though they possess several interesting properties (*e.g.*, spontaneous ignition in air when the amount of "mischmetall" is of the order of 10–16 per cent.).

As regards the *theory* of pyrophoric properties, it need only be said here that it is supposed that in striking the alloy small particles of the metal are broken off, and that the force of percussion involved in this is sufficient to raise these to their ignition point.

With regard to the *use* of pyrophoric alloys, it should be noted that whilst by far the greater proportion of alloys goes towards the manufacture of lighter flints, etc., considerable quantities are also employed in ballistics studies (for example, for definition of the flight of shells) and—because of the extreme reactivity of "mischmetall"—for the reduction of certain refractory oxides, such as those of niobium, tantalum, and zirconium.

A second use for **cerium salts,** and one that is becoming increasingly important, relates to the "coring" of carbon arc electrodes. Two salts, in particular, are employed for this purpose. The first is cerium fluoride ($2CeF_3.H_2O$), which—generally in its anhydrous form—is frequently mixed with calcium fluoride and a small quantity of sodium phosphate or borate in order to increase the fusibility of the mixture. According to an old French Patent (431,040, 1911), a suitable coring mixture may contain the fluorides of other rare elements, together with compounds of alkali metals with tungsten or molybdenum.

The second salt, cerium titanofluoride (*cf.* British Patent 13,988, 1912) is used in a similar manner, but with this substance it has been found necessary to add sodium or potassium fluoride in order to "steady" the flame. The colour imparted to the flame by the sodium or potassium salt is corrected by the further addition of a barium compound, and in order to minimise the etching effect of the fluorides on the surrounding glass, a small percentage of either silicate, tungstate, carbonate, or molybdate of sodium is also added.

A typical core analysis, relating to a modern British 15.8 mm. diameter carbon electrode (nominal diameter = 16 mm.), is given below:

Total rare earths oxides	45.00	per cent.
Thoria	0.63	"
Ceria	20.70	"
Ferric oxide	0.16	"
Alumina	0.34	"
Calcium oxide	0.85	"
Fluorides	11.20	"
Silica	0.27	"
Sulphates	4.60	"
Silicon carbide	0.78	"
Phosphates	0·96	"
Rare earths as metals	37·70	"
Carbon	43·40	"

(The ash content of the shell amounts, in this case, to 0.54 per cent., and the porosity of the shell to 21.4 per cent.)

Minor uses of cerium derivatives in industry are as follows:—

In the **textile industries,** cerium oxide (mixed with tin compounds) is used for weighting silk, and cerous chloride (a strong reducing agent) for rendering cloth resistant to mildew, and for producing variegated patterns on textiles, such as cotton. For this last-named purpose, the yarn is impregnated with a solution of cerous chloride (sp. gr. 1.16–1.26), dried and passed through a bath of strong sodium hydroxide. It is then dried again, woven to pattern with untreated yarn, dyed with a direct cotton dye, and finally run through an acid bath in which the treated fibres lose their colour. The reverse change can be produced by using "vat" or "thio" dyes in place of the direct cotton dyes.

In the **dyestuffs industry** itself, cerium earths are employed as a base for alizarin dyes and the acid sulphate of cerium ($Ce(HSO_4)_3$, which is produced by heating cerous sulphate with moderately strong sulphuric acid) has been recommended as an oxidising catalyst in the manufacture of aniline black. 0.3 gm. of cerous oxide, Ce_2O_3, when converted into the acid sulphate, are reported to be sufficient to develop the black from 6 kg. of aniline hydrochloride.

Cerium salts are also used as mordants in the **dyeing of leather.** In the preparation of leather, the hide partially reduces ceric sulphate or ceric ammonium nitrate, and thus yields a yellow-tinted product that is resistant to water.

Medicinally, cerous oxalate and double ammonium citrate, tartrate, and lactate find use in the treatment of sea-sickness, nausea, and nervous disorders.

In **photography,** cerium sulphate has been recommended as useful for reducing the density of negatives (*cf.* German Patent 123,017), and for rendering paper sensitive to light; cerium nitrate has been similarly employed. In both cases, the image produced on such sensitised paper can be developed with phenol or amido-benzoic acid.

Small quantities of cerium salts are finally used for colouring glass, as oxidising catalysts in organic preparations, and in the manufacture of incandescent gas mantles.

Estimation of Cerium in Minerals and Alloys.

(*a*) **Gravimetric Methods.**—Because of the presence of associated earths and other impurities, the estimation of cerium is usually a lengthy (and not standardised) procedure. The following can therefore only be regarded as a guide.

The first step in the analysis generally involves heating the mineral with sulphuric acid or fusing it with potassium bisulphate; extracting the residue with water; and precipitating thorium and cerium earths from the aqueous extract in the form of the oxalates. These are then filtered, decomposed with fuming nitric acid, and cerium finally converted into its insoluble hydroxide and isolated. This may be done in several ways.

For example, the *mixed* hydroxides are suspended in a 5 per cent. solution of KOH, and a current of chlorine passed through this suspension until it is no longer alkaline and the precipitate has assumed a yellow colour. This treatment causes cerium to be precipitated as the insoluble ceric hydroxide whilst the remaining cerium earth metals pass into solution as chlorides or hypochlorites. The ceric hydroxide is then filtered off, dissolved in hydrochloric acid and the procedure repeated. Finally, the pure hydroxide is reconverted into the oxalate, ignited to ceria, and weighed.

According to an alternative method, the mixed nitrates are neutralised with sodium carbonate, heated to boiling, and treated with a solution of potassium permanganate until a permanent faint pink colour is developed. A mixture of potassium permanganate and sodium carbonate is then run into the solution until an excess of permanganate is present, the precipitated hydroxides of cerium and manganese filtered off and washed, dissolved in hydrochloric acid, and the treatment repeated. The precipitate finally obtained is then again dissolved in hydrochloric acid and cerium separated from manganese by precipitation as the oxalate, which is then ignited and weighed as ceria.

(*b*) **Volumetric Method.**—Volumetric estimation of cerium in the presence of lanthanum and didymium is based upon the fact that ceric salts are reduced to cerous salts by hydrogen peroxide, and that ammonium persulphate in sulphuric acid solution causes the reverse change. Accordingly, to the solution of cerous salts in dilute sulphuric acid, one adds 2 gm. of ammonium persulphate, heats to boiling, cools to 50° C.; adds a further 0.5 gm. of persulphate, and repeats the procedure two or three times. Finally, the solution is heated for 15 minutes with more sulphuric acid in order to decompose excess persulphate, and cooled. Excess standard solution of hydrogen peroxide is then added, and the mixture back-titrated with potassium permanganate solution. The reduction of the ceric salt may be represented by

$$2CeO_2 + H_2O_2 = Ce_2O_3 + O_2 + H_2O.$$

REFERENCES

(1) G. Martin, "Pyrophoric Alloy Industry," *Chem. World*, **2**, 288 (1913).
(2) C. M. Dyson, *Ind. Chem.*, **7**, 231 (1931).
(3) S. B. Roy, *Chem. and Ind.*, **52**, 745 (1933).
(4) W. J. Bartlett, *Ind. Eng. Chem.*, **21**, 970 (1929).
(5) A. St. John, Am. Inst. Min., Tech. Pub. 22 (1927).

SECTION LXXVIII

TITANIUM

By Norbert Berkowitz

LITERATURE

"Distribution and Use of Titanium Ores." *Bull. Imp. Inst.*, 9 (1911).
F. L. Hess.—"Titanium." *Min. Res. U.S.A.*, Pt. I. 1911.
P. Pascal.—"Traité de Chimie Minérale," Vol. V. 1932.
C. S. Dumont.—"Bibliography on Titanium: its Production, Properties and Uses." Batelle Memorial Inst., Ohio, U.S.A., 1947.
J. Barksdale.—"Titanium: its Occurrence, Chemistry and Technology." Ronald Press Co., New York, 1949.
F.I.A.T. Final Report 773.—"Titanium Products in Germany."

Titanium (Ti = 47.90; atomic number 22), although still frequently regarded as a rare metal, is, in fact, the ninth element in order of abundance. It occurs naturally either as the **dioxide** TiO_2 (as in the minerals rutile, anatase, brookite, and ilmenite) or in association with various **silicates** (as in the "titano-silicates" sphene, perovskite, johnstrupite, neptunite, leucosphenite, rinkite, etc.).

Rutile (ordinary variety) usually occurs as a reddish-brown tetragonal mineral containing between 98 and 99 per cent. TiO_2 and 1–2 per cent. ferric oxide, Fe_2O_3, and having a specific gravity of 4.18–4.25. Black varieties of rutile (such as nigrine, ilmeno-rutile and strüverite) are heavier (sp. gr. about 5.1) and represent ferriferous forms containing substantial proportions of ferrous tantalates and niobates in addition to TiO_2.

Anatase (also known as octahedrite) corresponds to the ordinary variety of rutile as regards composition and principal crystal habit, but is somewhat lighter (sp. gr. 3.82–3.95). The colour of anatase varies from brown to indigo-blue (and occasionally jet black).

Brookite forms orthorhombic crystals consisting of almost pure TiO_2, but the colour of this mineral is usually lighter than that of rutile or anatase, varying from yellow to reddish. (An iron-black variety has also been described, but this is relatively rare.)

Ilmenite (or menaccanite) is a titaniferous iron ore normally containing Ti : 31.6 per cent., Fe : 36.8 per cent., and O : 31.6 per cent. Small quantities of magnesium may, however, sometimes replace part of the iron. The specific gravity of Ilmenite is 4.5–5.0 and the colour almost invariably iron black.

Among the titano-silicates, only **sphene** (or titanite) needs to be mentioned. This mineral forms monoclinic crystals possessing a specific gravity of 3.4–3.56 and a composition corresponding, in the usual varieties, to $CaO.TiO_2.SiO_2$ ($= SiO_2$: 30.6 per cent., TiO_2 : 40.8 per cent., CaO : 28.6 per cent.). In some varieties, however, part of the calcium may be replaced by iron, manganese, or yttrium. The colour of sphene varies from yellow to rose red (when containing Mn) and black (when containing relatively high proportions of iron). Two greenish forms (spinthère and ligurite) have also been described.

Geographical Distribution of Titanium Ores. Owing to the very large number of Ti-bearing minerals—46 have so far been reported—and to their very wide dissemination (sometimes as secondary minerals in igneous rock masses), no complete account of their distribution is possible here. Only the most important deposits are therefore mentioned.

(*a*) **Rutile and Related Ores.**—In **Europe,** prominent rutile deposits occur in Austria (Styria, Tyrol, and Carinthia); in Switzerland (Grisons, Valais, St Gotthard, Binnenthal, etc.); in France (near Limoges); and in Norway (at Kragerö, Snarum, Risör, etc.). In the **U.S.A.**, workable deposits have been found in Vermont (near Waterbury) and at various localities in Connecticut, Massachusetts, New York, Arkansas (near Hot Springs), and Virginia (notably in the counties of Amherst and Nelson). Smaller deposits have also been reported in Adelaide Co. (South Australia); in the beach sands of Northern Australia, and at several places in Brazil and Madagascar. Ilmeno-rutile and struverite (two black varieties of rutile) occur mainly in the Ilmen mountains of Russia and near Piedmont in Italy respectively. Rich deposits of ilmenite, with zircon and rutile have recently been proved at Umgababa, near Durban (1952), and these ores will be mined there in the near future. The quantities of ore said to be proved include 2,000,000 tons of ilmenite, 200,000 tons of zircon, and 100,000 tons of rutile.

(*b*) **Sphene and Related Titano-Silicates.**—The most important deposits of titano-silicates occur frequently at or near the major rutile deposits. In **Europe,** massive sphene is thus found in Austria (notably in the Zillerthal of Tyrol); in Italy (Trentino); in Switzerland (Grisons, St Gotthard, Binnenthal, Zermatt, etc.); in France (Maronne); and in Norway (Kragerö, Risör, and Arendal). In the **U.S.A.**, deposits of sphene and other titano-silicates have been located in Arkansas (near Hot Springs in Garland Co.); in New York (near Natural Bridge in Lewis Co., and at various points in St Lawrence and Orange counties); and in New Jersey (at Franklin in Sussex Co.). Minor deposits occur in Canada (at Litchfield in Quebec, and in Ottawa Co.); in the Ural Mountains in Russia; in Madagascar and in Brazil.

Preparation of Metallic Titanium.—Metallic titanium, particularly if not required pure, can be obtained by reduction of the dioxide with calcium in the presence of calcium chloride, or with calcium hydride. Calcium oxide is then removed by treatment with dilute acids, and the residual solid exhaustively washed with water, dried, moulded into cubes or bars, and sintered *in vacuo* in an induction furnace. The resultant metal is, however, rather brittle owing to the incomplete elimination of oxides and nitrides.

It is therefore generally more convenient to extract the metal by:

(*a*) electrolysis of potassium fluotitanate, K_2TiF_6, in a fused alkali chloride or fluoride bath,
(*b*) interaction of titanium tetrachloride with Na in a bomb, or
(*c*) by reduction of the dioxide with magnesium *in vacuo*.

(Titanium tetrachloride ($TiCl_4$), required for (*b*) is readily prepared by treating TiO_2 with carbon in a stream of dry chlorine. It is a colourless, fuming liquid that is partly hydrolysed by water.)

Of these three processes, the first and second yield metallic titanium of up to 99.9 per cent. purity, and this can be pressed and hot-worked into rods and plates. The third method, which is similar to the calcium reduction method, is superior to it since it produces a malleable metal that is substantially free from oxides and nitrides.

On a small scale, very pure malleable Ti can also be made by decomposing titanium tetraiodide (TiI_4) on a heated tungsten or titanium filament.

Properties of Metallic Titanium.—Pure titanium metal is a dark-grey powder when amorphous, and white (and isomorphous with zirconium and silicon) when crystalline. The fused metal somewhat resembles polished steel, and is sufficiently hard to scratch quartz (hardness number 7 on Moh's scale). When rubbed against steel it emits a shower of bright sparks.

In the cold, titanium is brittle and can be powdered with little effort; it can, however, readily be forged and drawn at bright red heat if it is free from carbide. When heated in air, practically no oxidation occurs up to about 120° C., at higher temperatures the surface rapidly becomes coated with a mixture of oxide and nitride, and the metal finally melts at 1,800° C. (3,272° F.).

When titanium metal is heated in oxygen it ignites at about 610° C., to burn with exceptional brilliance to form TiO_2. Because of this, the metal has found some use in pyrotechnics.

Titanium is, incidentally, also the only element to burn vigorously when heated in nitrogen; ignition occurs at 800° C., and the main product is titanium nitride, TiN.

The specific heat of Ti is 0.1125 over the range 0°–100° C. or 0.162 over the range 0°–450° C.; its specific gravity 4.5; and its specific resistance 80 microhms/cu. cm. at 0° C. (Clausing and Moublis, 1927). The coefficients of linear expansion per °C. for 97.2 per cent. pure Ti are

5.0×10^{-6} at $-150°$ C. (P. Hidnert, 1943),
8.2×10^{-6} between 20° and 300° C. (J. D. Fast, 1939), and
12.0×10^{-6} at 650° C. (P. Hidnert, 1943).

Between 0° and 850° C., a value of 9.79 has been reported (W. Kroll, 1939).

Industrial Utilisation of Titanium and Ti Compounds.—The rapidly increasing number of uses to which titanium and its compounds are put in modern industrial practice is reflected in the total tonnages of Ti ores produced in 1913 and 1949. Thus, whilst world production prior to the first world war amounted to some 8,000 tons per annum, reports available at the time of writing quote figures of about 300,000 tons per annum.

By far the largest proportion of this quantity is used for the production of "titanium white" pigment (a chemically inert mixture consisting of TiO_2 and barium sulphate) and of a wide range of alloys in which the proportion of Ti varies from 0.2–75 per cent.

Titanium is a major constituent of a series of "ferro-titanium" alloys which are widely used as de-oxidisers and de-nitrogenisers in the manufacture of steels. These alloys are prepared by one of two general processes.

In the first (protected by Rossi in series of U.S. Patents between 1898 and 1912), finely pulverised titaniferous iron ore (Ilmenite) is mixed with charcoal and heated in an electric arc furnace to a temperature of not less than 1,927° C. (3,500° F.). The resultant product contains 15–18 per cent. Ti, 5–8 per cent. C, and the balance iron.

If a carbon-free alloy is required, the reduction is performed with aluminium scrap. High-grade iron ore and the requisite quantity of aluminium scrap is charged into an electric furnace and melted. Titaniferous iron ore is then added to the surface layer (which consists of aluminium) and heating continued until reduction and combination with the iron is complete. (This last stage is strongly exothermic, and only little extra current is required to maintain the bath temperature.) In this way, alloys containing up to 75 per cent. Ti and only 0.1–0.8 per cent. C can be produced.

Steels treated with ferro-titanium alloys are non-brittle and show no segregation of phosphorus and sulphur in the finished product.

As a minor constituent, titanium is also found in a range of aluminium and copper alloys. Chief among these is "Konel," an alloy consisting of ferro-titanium, nickel, and cobalt, and containing Ni 72.5 per cent., Co 17.0 per cent., Fe 7.5 per cent., Ti 2.5 per cent., and Si 0.5 per cent. This alloy is made by the Westinghouse Electric Manufacturing Co. (E. Pittsburgh, Pa., U.S.A.), and is claimed to be extremely tough at high temperatures (ultimate tensile strength at 600° C. = 27 tons sq. in.). It is therefore advantageously used in movable parts of internal combustion engines. It is noteworthy that "Konel" was originally developed as a substitute for platinum in the manufacture of filaments for radio-valves; such filaments have a far longer life period and enable the valves to be operated at a temperature some 175° C. below that required for valves fitted with platinum. Correspondingly improved reception has been claimed.

In copper alloys, the addition of a small quantity of titanium (up to 0.5 per cent.) results in greatly improved casting and age-hardening properties. Ti treated copper alloys can thus be cast in sand without difficulty, and since titanium will also remove oxides and occluded gases, very closely structured castings free from blow-holes can be obtained in this way.

A more recent development is the use of titanium (about 0.04 per cent.) to replace vanadium (about 0.10 per cent.) in high-strength weldable steel plate used for construction of ships hulls. It is claimed that Ti-bearing steel plate is cheaper to produce than V-bearing plate, and that it is rather more ductile, more corrosion resisting, and less susceptible to strain-age-embrittlement.

For similar reasons, titanium serves to replace part of the vanadium in high-speed tools.

Because of its strong affinity for carbon, and the low solubility of the carbide in solid steel, titanium also affords a useful constituent in chrome-nickel stainless steels.

A new application of titanium has also been found in arc welding, where the use of ferro-titanium in the electrodes in place of silicon or manganese assists in the de-oxidation of the weld. The titanium dioxide produced forms a slag that can readily be stripped off. It is estimated that consumption of rutile for this purpose alone amounts to between 1,500 and 2,500 tons per annum (1949).

With the recent greater availability of pure titanium ores, particularly rutile, the use of the metal itself as a constructional material becomes more possible. The tensile strength of the metal is nearly twice that of mild steel, whilst its density is about two-thirds that of steel. With its improved resistance to corrosion, the value of titanium as a constructional material for aeroplanes, motor cars, and ships is therefore extremely great, though its value is hardly the £14,000 per ton for which the metal has been sold recently.

Metallic titanium has been recommended as a constituent for cerium-free pyrophoric alloys. According to a French Patent (No. 419,388, 1910) still being worked, a suitable mixture contains at least 10 per cent. of manganese and antimony, 20 per cent. or less of chromium, and 10–15 per cent. titanium.

Among titanium compounds, industrially the most important is the carbide, TiC, which forms when the metal is heated in an electric arc and allowed to absorb carbon. This material is harder than carborundum and has been used for the production of a hard alloy (consisting of 50 per cent. TiC and 50 per cent. TiN) suitable for cutting tools (Krupp, D.R.P. 365,895, 1931). In the form of a titanium-tungsten carbide, corresponding to the formula $W_2Ti_2C_4$, it has also been used for tipping high shock-resistance tools, and for the manufacture of nozzles, valve seatings, and die inserts. An example is provided by "Cutanit," an alloy containing up to 10 per cent. TiC, 5–13 per cent. Co, and the balance tungsten carbide.

Several titanium compounds are further used in the textile and leather industries. Thus, titanous chloride, $TiCl_3$, and titanous sulphate, $Ti_2(SO_4)_3$, have found extensive application as stripping agents, *i.e.*, for removing dyes from unevenly dyed (or stained) fabrics. They appear to be particularly useful for stripping "Primuline yellow," "Thioflavine S," and iron mould stains.

In the leather industry, potassium titanium oxalate is employed both as a mordant and as a dye (since it combines with the tannin to give a fast yellow to brown titanium tannate), and basic sodium titanium sulphate has found application for tanning. Titanium lactates have also been used as mordants; the required solutions are prepared by reacting freshly precipitated titanium hydroxide with lactic acid and an alkali, or, if an excess of lactic acid is undesirable, by treating a solution of titanium chloride, sulphate, or oxalate with an alkali lactate.

For wool, a suitable mordant is provided by a solution of $TiCl_4$ and cream of tartar.

Titanium compounds have also found wide use as pigments and constituents of protective paints. Apart from "titanium white" pigment, which has already been referred to, a range of pigments varying from yellow to red can thus be obtained by roasting titaniferous iron ore under controlled conditions (French Patent 412,563, 1910). A yellow pigment which has been stated to be suitable for use in rust-prevent paints, has also been manufactured by heating titaniferous iron ore with sulphuric acid and subsequently decomposing the sulphates so formed at some higher temperature (British Patent 10,368, 1911). Recent work on Ti pigments and enamels (carried out in Germany) has been described in F.I.A.T. 773.

It is of interest that several of these pigments are used in the ceramic industries to give a soft yellow underglaze to porcelain ware, and that titanium dioxide itself has been found to improve fused quartz articles.

The most recent application of TiO_2 relates to the preparation of **semi-conducting materials.** Thus, "Urdox" resistors, manufactured by the Siemens Telefunken Laboratories, contain a mixture of TiO_2 and MgO, and have an electrical resistance that follows an inverse logarithmic law when plotted against absolute temperature. It is claimed that these resistors introduce a minimum of thermal noise when used in electronic circuits. Thin films of, or containing, TiO_2 are also said to show very high thermal e.m.f.'s (more than ten times those of metals); their decreasing resistance with rise in temperature, combined with low heat capacity, suggest therefore that such films might be used in measuring radiant energy and very low gas pressures (Pertinent German Patents are listed in F.I.A.T. Final Report No. 773).

Analysis of Titanium Ores.—The method of estimating titanium in ores depends largely upon the nature of the other constituents present in them.

Case I: Tungsten and Vanadium absent.
Chromium < 3 per cent.

Dissolve 1 gm. sample (2 gm. if Ti < 0.25 per cent.) in 50 c.c. warm, dilute H_2SO_4 (1 : 6), oxidise by dropwise addition of nitric acid (sp. gr. 1.42), and boil to expel nitrous fumes. Then filter and wash with hot dilute H_2SO_4 (1 : 10). Transfer residue to a platinum crucible, ignite at 650° C., cool and add 1 c.c. dilute H_2SO_4 (1 : 4) and 2 c.c. hydrofluoric acid. Finally, evaporate to dryness, fuse the residue in 2 gm. potassium bisulphate at a low temperature until a clear liquid is obtained, and extract the cooled melt in the original filtrate.

Prepare a blank solution for comparison by treating a titanium-free steel as described above. (If the Ti ore contains Ni, Cr, Co, or Mo, add equivalent quantities of the sulphates[1] of these metals to the blank solution.) Transfer the two solutions to graduated comparison cylinders, add 10 c.c. dilute phosphoric acid (1 : 1) and 5 c.c. H_2O_2 (10 vols.) to each, and slowly admit standard titanium solution to the blank until the colour intensities of the blank and ore are identical at equal dilution. If $N =$ number of c.c. of standard titanium solution added to the blank, and $W =$ weight of ore used,

$$\text{Percentage Ti in ore} = 0.10N/W.$$

(To prepare the standard 0.10 per cent. titanium solution, dissolve 7.40 gm. titanium potassium oxalate in 60 c.c. H_2O, add 40 c.c. H_2SO_4 (sp. gr. 1.84) and evaporate until fumes begin to be evolved. Then cool, dilute with H_2O to a total volume of 200 c.c. and warm gently. Filter, wash the solid residue on the filter with dilute H_2SO_4 (1 : 9) and make up the filtrate to 1,000 c.c. The true Ti content of the solution can be checked by precipitating Ti from a 50 c.c. aliquot with NH_4OH in the presence of 5 gm. NH_4Cl, filtering, washing the precipitate with hot water, and finally igniting to constant weight of TiO_2 (Ti in $TiO_2 = 59.95$ per cent.). 1 c.c. of the solution should contain 0.001 gm. Ti.)

---

[1] If Mo > 0.5 per cent., add its equivalent as ammonium molybdate solution.

Case II: Tungsten, Vanadium, etc., present.

Use the cupferron precipitation method: dissolve 1 gm. of sample (*cf.* note 1) in 50 c.c. dilute H_2SO_4 (1 : 4) (*cf.* notes 2 and 3), dilute, cool, add a little paper pulp and slowly admit an aq. 6 per cent. cupferron solution until the precipitate just turns a faint reddish-brown colour. Allow to stand for five minutes; then filter. Wash the precipitate with cold 5 per cent. H_2SO_4 containing 1 c.c. of the cupferron solution per litre, and follow up with several portions of cold 5 per cent. NH_4OH. (This last step can be omitted if tungsten, copper, and molybdenum are known to be absent.) Transfer the precipitate to a platinum crucible, and ignite at 650° C. Cool, add 2 c.c. dilute H_2SO_4 (1 : 4) and 5 c.c. hydrofluoric acid, evaporate to dryness, fuse residue in 2 gm. potassium bisulphate at a low temperature until a clear melt is obtained, and extract with dilute H_2SO_4 (1 : 6) (*cf.* note 4).

Prepare a blank solution by fusing 2 gm. potassium bisulphate and extracting as above; then proceed as under Case I, omitting addition of the phosphoric acid.

Notes.—

1. With Ti $<$ 0.3 per cent. use 2–5 gm. of sample.
   With Ti $>$ 0.7 per cent. use 0.5 gm. of sample.
2. If the ore shows a carbide residue that is insoluble in dilute H_2SO_4, evaporate until fumes just appear, cool, add 10 c.c. H_2SO_4 (1 : 4) and dilute with H_2O to 100 c.c. Then warm until all salts are in solution.
3. If the ore contains vanadium, proceed as under note 2, and treat with 50 per cent. NH_4OH until a faint permanent precipitate appears. Then add 20 c.c. sat. sulphurous acid and bring to the boil. Boil for two minutes, cool, adjust to 10 per cent. acidity with 50 per cent. H_2SO_4, and cool again.
4. If copper is present in sufficient quantities to colour the solution, precipitate the Ti with NH_4OH and wash with dilute (2 per cent.) NH_4OH. Then repeat ignition, fusion, and extraction of the melt.)

In the absence of compounds that are oxidised by ferric salts (*e.g.*, salts of niobium, vanadium, or uranium) titanium can, incidentally, also be determined by reducing it to $Ti^{\cdot\cdot\cdot}$ with zinc and a strong acid, and titrating the solution with ferric alum in an inert atmosphere. Ammonium thiocyanate is used as indicator.

Prices.—Current (1940) U.K. prices of rutile ($TiO_2 < 95$ per cent.) range between £50 and £60 per ton. U.S.A. prices of ferro-titanium vary from \$1.25 to \$1.45 per lb. of contained titanium.

REFERENCES

(1) W. M. Thornton, Jr., "Titanium, with special reference to analysis of titaniferous substances." Amer. Chem. Soc. Monograph (1927).

(2) D. R. Block, Dissertation, Faculty of Science, Columbia College, U.S.A., 1930. (Dealing with analysis of titaniferous substances.)

(3) F. M. Becket and R. Franks, "Titanium and Niobium in High Cr Steels." Amer. Inst. Min. Engin., Tech. Publ. No. 506 (1933).

(4) E. W. Washburn and E. N. Bunting, "Note on Phase-equilibrium in the system $Na_2O - TiO_2$." U.S. Bur. Stand., *Journal of Research* XII (1934).

(5) J. R. Thoenen and J. O. Warne, "Titanium Minerals in Central and N.E. Florida." U.S. Bur. Mines, Rep. Invest. 515 (1949).

(6) L. E. Ross and C. A. Tanner (Amer. Cyanamide Co.), "Production of Rutile TiO_2." U.S. Patent 2,494,492 (1950).

(7) H. Jaffe, "Titanate Ceramics for Electromechanical Purposes," *Ind. Eng. Chem.*, **42**, 264 (1950).

(8) P. H. Brace, W. J. Hurford, and T. H. Gray, "Preparation and Properties of Ti-base alloys," *Ind. Eng. Chem.*, **42**, 227 (1950).

(9) E. I. Larsen, E. F. Swazy, L. S. Busch, and R. H. Freyer, "Fabrication of Ti-rich alloys," *Ind. Eng. Chem.*, **42**, 237 (1950).

(10) W. H. F. Tickle, "The Self-Opacification of Ti enamels," *Proc. Inst. Vitreous Enamel*, **8**, 78 (1943-47).

(11) R. T. Runnels, M. G. Utter, and A. C. Read, "Determination of Fe_2O_3 and TiO_2 in presence of Al_2O_3," *J. Amer. Ceram. Soc.*, **33**, 51 (1950).

(12) E. H. Goda (Furo-Enamel Corporation), "Refining of Rutile." U.S. Patent 2,496,993 (1950).

(13) G. Bieler, "Titanium in Enamelling," *Silicates Ind.*, **15**, 29 (1950).

(14) A. L. Friedberg and F. A. Petersen, "Systematic Study of simple TiO_2-bearing Porcelain Enamels," *J. Amer. Ceram. Soc.*, **33**, 17 (1950).

(15) G. H. Spencer-Strong and R. F. Patrick, "Titanium in Porcelain Enamels," *Ind. Eng. Chem.*, **42**, 253 (1950).

(16) R. T. MacMillan, J. I. Dinnin, and J. E. Conley, "Proposed Process for treatment of low-grade titaniferous ores." U.S. Bur. Mines, Rep. Invest. 4638 (1950).

(17) G. Durst, M. Grotenhuis, and A. G. Barkow, "Solid Solubility Study of Ba, Sr, and Ca titanates," *J. Amer. Ceram. Soc.*, **33**, 133 (1950).

(18) B. T. Matthias, "New Ferro-electric Crystals," *Phys. Rev.*, **75**, 1771 (1949).

(19) L. C. Copeland and C. W. Farber (New Jersey Zinc Co.), "Production of Titanium Dioxide." U.S. Patent, 2,486,465 (1949).

(20) A. I. Dranetz, G. N. Howatt, and J. W. Crownover, "Barium Titanates as Circuit Elements," *Tele-Tech.*, **8** (5), 28 (1949).

(21) M. M. Fine, H. Kenworthy, R. B. Fisher, and R. G. Knickerbocker, "Titanium Investigations: Laboratory Development of Mineral Dressing Methods for Arkansas Rutile," *Min. Engin.* (*Trans.*), **184**, 447 (1949).

(22) E. Wainer (National Lead Co.), "Synthetic Rutile and Methods of Making Same." U.S. Patent, 2,489,246 (1949).

(23) L. A. Thomas, "Ferro-electric Ceramics," *Times Rev. Ind.*, **3** (30), 25 (1949).

(24) D. R. Goetchius, "Review of Titanium Enamel Development and its General Properties," *Enamelist*, **26** (4), 3 (1949).

SECTION LXXIX

ZIRCONIUM

By Norbert Berkowitz

LITERATURE

P. Pascal.—"Traité de Chimie Minérale," Vol. V, 1932.

F. P. Venables.—"Zirconium and its Compounds," Amer. Chem. Soc., Monograph Series, 1922.

E. P. Youngman.—"Zirconium, General Information," U.S. Bur. Mines, Information Circ. No. 6455, 1931.

F.I.A.T. 1048.—"Production of Zirconium Oxide."

F.I.A.T. 617.—"The Electrical and Technical Ceramic Industry in Germany."

Like titanium, to which it is chemically closely related, zirconium (Zr; atomic weight = 91.22; atomic number = 40) is a "rare" element only by courtesy (and possibly because of its somewhat limited applications); in order of abundance it is nineteenth, being more than twice as plentiful as copper, and more than twelve times as abundant as lead.

It occurs naturally, mainly as the ortho-silicate (Zircon), or as the dioxide (Baddeleyite), but it should be noted that it also forms an important, and often major, constitutent of several other minerals (*e.g.*, **Wöhlerite,** a zirconium-silicate and niobate of Ca, Na, etc.; **Lävenite,** a complex zirconium silicate of Mn, Ca, etc., and also containing Ti, Ta, F, etc.; and **Zirkelite,** a mixed oxide corresponding to the empirical formula (Ca, Fe) (Zr, Ti, Ta)$_2$O$_5$.

Zircon, when pure, contains about 67.2 per cent. ZrO_2 and 32.8 per cent. SiO_2, but most varieties contain a small quantity of iron (as Fe_2O_3) and combined water, and some (*e.g.*, Hagatalite, a variety occurring in Japan) may contain up to 4 per cent. of hafnia. It is usually found as a brown opaque mass with pronounced conchoidal fracture and adamantine lustre; its hardness number is 7.5, its specific gravity 4.68–4.70, and its colour pale yellow-grey to reddish-brown. Transparent forms of zircon ("hyacinth") are relatively rare and have been used as semi-precious stones.

Baddeleyite has a rather less well-defined composition than zircon and may contain anything between 69 per cent. and 99 per cent. ZrO_2 (*cf.* Table I). It normally occurs in the form of tabular monoclinic crystals with a hardness number of 6.5 and a specific gravity of 5.5–6.0. Its colour ranges from very faint grey to brown and black.

Geographical Distribution of Zirconium Ores.—By far the most common and widely distributed of the Zr ores is Zircon. In **Europe,** substantial deposits of this mineral have been reported in Russia (Ilmuren and Ural mountains); in Italy (Trentino, Pfitschtal, and at Mte. Somma); in France (Haute-Loire); and in Norway (Kragerö, Langesundfiord region, and Vestfold). In the **U.S.A.,** massive deposits occur in Maine, Massachusetts (Chesterfield), New York (counties of Essex, Orange, and St Lawrence), North Carolina, and Colorado. The mineral has also been found in Canada (Ontario and Quebec); in the alluvial sands of Ceylon; and in Madagascar (Betroka and Mt. Ampanobe): more recently a rich source of zircon has been found in the beach sands of North Australia.

Baddeleyite is relatively rare, and substantial occurrences have so far only been reported from Italy (Mte. Somma, Vesuvius), Sweden (Alnö), Ceylon, and Brazil (São Paulo).

Extraction of Metallic Zirconium from Zr Ores.—Since metallic zirconium combines readily with oxygen, nitrogen, carbon, silicon, etc., it cannot be prepared by reduction of the oxide with carbon; nor can satisfactory results be obtained by reduction of the oxide with lime, aluminium, or magnesium. (F. Wedekind, *Annalen*, 395, 149, 1913). The most usual method of extraction involves, therefore, reduction of ZrO_2 by means of metallic calcium in the presence of calcium chloride, or alternatively, reduction with calcium hydride (*cf.* titanium). If commercial calcium of 95 per cent. purity is used, the metallic zirconium produced by the reduction process has a purity of approximately 97·7 per cent. An alternative method of manufacturing zirconium consists in reacting metallic sodium with the double potassium zirconium fluoride at a red heat.

In either case, the product is an amorphous black powder which is washed, dried, pressed into bars, degasified, and finally forged at about 900° C. As in the case of tungsten and tantalum, this is usually followed by a swaging and rolling process.

Pure zirconium metal melts at 1,850° C., has a specific gravity of 6.53 and a specific resistance (at 0° C.) of 41.0 microhms per cubic centimetre. (Clausing and Moublis, 1927). The thermal conductivity is 0.04 c. at 50° C., while the ultimate strength varies between 59,000 p.s.i. and 90,000 p.s.i., depending on the condition of working.

The metal is chemically extremely reactive to oxygen and, owing to its relatively low ignition temperature and high heat of combustion, has been used as an igniter in photo-flash bulbs, and as a constituent of ammunition primer compositions (see below).

It may be noted that **ductile** zirconium, suitable for the manufacture of sheet and wire, is now prepared industrially by thermal decomposition of zirconium tetraiodide (ZrI_4) on a thin wire heated electrically to about 1,300° C. This reaction is normally carried out in an evacuated pyrex glass apparatus into which porous (*i.e.*, amorphous) zirconium and a small quantity of iodine have been introduced. The process is described fully in *Metal Industry*, **54**, 164, 1939, and it is stated that the annual production of this form of zirconium amounts to nearly 1,000 tons.

Industrial Utilisation of Zirconium and its Compounds.—Metallic zirconium has so far only found limited application in industry. Its most important use to-day relates to the production of zirconium "master alloys," such as ferro-zirconium and silicon-manganese-zirconium. The former, containing about 20 per cent. of zirconium, is used in steel manufacture as a deoxidiser and denitrogeniser; the quantity of ferro-zirconium used for this purpose amounts to about 1 per cent. of the weight of steel to be treated. Silicon-manganese-zirconium is similarly used, but is also capable of removing sulphides and as acting as a grain refiner.

More recently metallic zirconium has been used as a minor alloying constituent in certain *high tensile alloy steels*, in which it induces increased ductility and shock resistance, and in *nickel-cobalt alloys*, where, used in conjunction with Mo or W, it produces excellent high speed steels.

An alloy containing 6.8 per cent. Zr, 53·5 per cent. Niobium (Columbium), and 39.7 per cent. Tantalum is also used as a substitute for platinum in the manufacture of corrosive-resistant chemical apparatus and instruments.

In the United States, a zirconium-nickel-silicon-iron alloy ($Zr = 2.7$ per cent.) has been introduced as an acid resistant alloy, and zirconium-copper alloys (containing 14-16 per cent. Zr) are beginning to compete seriously with copper-beryllium alloys.

Zirconium is also used in the construction of chemical plant for its corrosion-resisting properties. It is resistant to attack by most acids and bases, and forms a suitable material for chemical plant handling highly corrosive liquids.

Finally it may be noted that the metal itself finds, as already mentioned, some use in explosive compositions. Thus it can replace mercury fulminate or lead azide in electric blasting caps, and magnesium powder in flash-light compositions containing barium nitrate or potassium chlorate.

Among zirconium compounds that have found industrial application, the most important is zircon itself, which has been used for the manufacture of high temperature bricks. According to Hilliard and Stott, who have carried out most of the recent work on zircon, the dissociation of zircon at high temperatures (from 1,650° C. upward) can be overcome by refiring the artefacts at 1,500° C.; it is also claimed that the most satisfactory bricks can be made by using finely ground zircon as a bonding agent.

TABLE I

ANALYSES OF TYPICAL ZIRCONIUM MINERALS.

Constituent.	Zircon.		Baddeleyite.				
	Ceylon.	Norway.	Brazil, glassy.	Brazil, stony.	Brazil, pebbles.	Brazil, commercial.	Ceylon.
ZrO_2 - - -	66.35	64.05	93.12	88.40	74.48	68.93	98.90
Fe_2O_3 -	0.83	2.85	3.22	3.07	10.20	3.59	0.82
TiO_2 - - -	...	...	0.98	3.12	1.35	0.60	...
CaO - - -	...	...	...	...	...	...	0.06
SiO_2 - - -	32.35	32.53	2.41	5.89	14.08	26.30	0.19
H_2O - - -	0.23	...	...	...	...	0.80	0.28
Others - -	0.24	0.57	0.27	...	...	...	...
	100.00	100.00	100.00	100.48	100.11	100.22	100.25

Zirconia, ZrO_2, is similarly used as a refractory for lining crucibles, etc.; its incandescence in hot flames is considerably greater than that of lime or magnesia, and fireclay cylinders coated with zirconia have therefore been used in lighthouse lamps.

Minor Uses.—The use of various zirconium compounds as white **pigments** has been patented by L. Weiss (German Patent 235,495) as early as 1910. Among compounds specifically mentioned as suitable for this purpose are the oxide, silicate, basic carbonate, phosphate, and basic sulphite. All these are non-poisonous and are completely unaffected by hydrogen sulphide.

Basic zirconium acetate, or a mixture of soluble zirconium salts with sodium phosphate, have also been used for weighting silk (German Patent 232,875), and pure zirconia for defining intestines for X-ray photographs ("Kontrastin").

Prices of Zirconium.—The current price of pure zirconium metal is only slightly less than that of gold.

Analysis of Zirconium Ores.—Zirconium is usually estimated gravimetrically as the dioxide ZrO_2. If the ore under test is insoluble in acids it is fused with about five times its own weight of potassium bisulphate, the melt leached with a 2 per cent. solution of sulphuric acid, and the process repeated with any insoluble residue remaining after this treatment.

If the sample is directly soluble in acid, use 5 gm. and digest with about 75 c.c. of 25 per cent. sulphuric acid. Then proceed as follows: Transfer acid solutions to a large beaker, dilute to 150 c.c. with distilled water, cool to about 10° C. and carry out a Cupferron precipitation (see Case 2 of the analytical procedure applicable to titanium).

Then transfer the paper and precipitate to a platinum crucible, dry and ignite at 650° C. After cooling, add 2 c.c. of 50 per cent. sulphuric acid and 5 c.c. of hydrofluoric acid and evaporate to dryness. Fuse the resultant residue with 2 gm. of potassium bisulphate at a low temperature, cool again and extract the clear melt with 50–60 c.c. of 10 per cent. hydrochloric acid and 10 c.c. of a 50 per cent. solution of tartaric acid.

To the extract add dilute ammonium hydroxide solution (1 : 1) to make it slightly alkaline, and follow with 50 per cent. sulphuric acid to a final acidity of 1 per cent. by volume. Pass hydrogen sulphide through the solution for ten minutes (see note 1) and then add 15 c.c. of dilute ammonium hydroxide (1 : 1) under constant stirring. Continue passing hydrogen sulphide for a further ten minutes, stir in a little paper pulp, allow any precipitated ferrous sulphide to settle, and filter, washing the precipitate with freshly prepared ammonium sulphide. Acidify the filtrate with dilute sulphuric acid and boil to remove hydrogen sulphide (see note 2).

Add 10 c.c. of concentrated sulphuric acid for each 100 c.c. of solution, cool to 10°–15° C., add a little paper pulp and precipitate zirconium by dropwise addition of a 6 per cent. Cupferron solution until a fine white precipitate appears where the reagent meets the solution. Then filter carefully, wash repeatedly with cold 5 per cent. sulphuric acid containing a little Cupferron solution (see note 3), dry the precipitate in a weighed platinum or silica crucible, and ignite at a low temperature which is gradually raised to 1,000° C., cool and weigh the crucible. The percentage of zirconium is then given by

$$\text{percentage Zr} = \frac{B - A \times 0.7403}{\text{Wt. of sample taken}}$$

where $B - A$ = weight of zirconia (see note 4).

Notes.—

1. If molybdenum or copper are observed at this stage, filter, wash with dilute sulphuric acid (1 per cent.) saturated with hydrogen sulphide, and treat the filtrate with hydrogen sulphide for three minutes. Then proceed, as indicated, with ammonium hydroxide.
2. Heating must be carried out very carefully in order to prevent the solution from bumping or suddenly boiling over.
3. If the sample is known to contain tungsten, washing of the Cupferron precipitate should be carried out with four separate quantities of cold 5 per cent. ammonium hydroxide solution.
4. It should be noted that this residue will contain any titanium that may be present. This may be determined colorimetrically as described in Section LXXVIII and the weight of titania so determined subtracted from the weight of the impure zirconia.

REFERENCES

(1) J. A. M. van Liempt and J. A. de Vriend, "Untersuchungen uber das Zirkoniumlicht," Philips' Gloeilampenfabrieken, Separaat 901 (1934).

(2) W. J. Baldwin, "Fireproof Bricks from Zirconium Silicate and Zirconia," *Chem. Eng. Progr.*, **44** (11), 875 (1948).

(3) V. H. Stott and A. Hilliard, "Variation in the Structure of Zircon," *Min. Mag.*, **27**, 198 (1946).

(4) —— "Zircon Refractories," *Trans. Brit. Ceram. Soc.*, **48**, 133 (1949).

(5) A. Hilliard, M. Pirani, and CURA Patents Ltd., "Improvements in the Manufacture of Refractory Materials," British Patent 607,317 (1948).

(6) J. H. McKee and A. M. Adams, "The Physical Properties of Slip-cast Zircon with Reference to Thermal Shock Resistance," *Trans. Brit. Ceram. Soc.*, **49** (9), 386 (1950).

(7) R. F. Geller and P. J. Yavorsky, "Thermal Dissociation of Zircon," *J. Res. Nat. Bur. Stand.*, **35**, 87 (1945).

(8) D. L. Deadmore, "Effect of Thermal Shock and Annealing on certain Physical Properties of a Zircon Body," *Ceramic Age*, **55**, 17 (1950).

(9) Titanium Alloy Manufacturing Co., "Improvements relating to the Methods of Making Insulators and to Ceramic Compositions," British Patent 634,181 (1950).

(10) Russian Standards Committee, "Classification of Refractory Products," Russ. Stand. G.O.S.T. 4385–48 (1948).

(11) W. B. Blumenthal, "Zirconium Compounds in Industry," *Chem. Trades J.*, **126**, 169 (1950).

(12) E. A. Gulbrausen and K. F. Andrew, "Mullite and Zircon Furnace Tubes for High Temperatures and High Vacuum Systems," *Ind. Eng. Chem.*, **41**, 2762 (1949).

SECTION LXXX

TANTALUM AND NIOBIUM

By Norbert Berkowitz

LITERATURE

P. Pascal.—"Traité de Chimie Minérale," Vol. IV, 1932.

W. Schoeller.—"Analytical Chemistry of Tantalum and Niobium." London, 1937. (Published under auspices of Society of Public Analysts.)

M. M. Austin.—"Working Properties of Tantalum." Amer. Inst. Min., Tech. Publ. No. 278, 1930.

W. G. Burgers and J. C. M. Basart.—"Darstellung von duktilem Tantalum durch chemische Dissoziation von $TaCl_5$." Philips' Gloeilampenfabrieken, Separaat 845, 1934.

"References to the Industrial Application of Niobium." Science Libr. Bibliogr. Series No. 238, 1936.

TANTALUM

Tantalum (Ta; atomic weight = 180.88; atomic number = 73), a member of the bismuth group of metals, occurs as the pentoxide Ta_2O_5 in more than forty minerals, but is normally only extracted from Tantalite and Columbite.

Tantalite is a black mineral crystallising in the orthorhombic system, and may contain as much as 70 per cent. Ta_2O_5. Its composition corresponds to that of an iron tantalate containing a small proportion of manganese. Its specific gravity varies between 6.5 and 7.3.

Columbite (specific gravity 5.3–0.5) is isomorphous with tantalite and frequently associated with it, but consists mainly of iron-manganese niobate; the tantalum content of columbite does not normally exceed about 10 per cent.

Tantalite and Columbite are thus the extremes of a series of minerals in which Ta_2O_5 is progressively replaced by Nb_2O_5.

Other tantalum-bearing minerals containing high proportions of the metal are **Fergusonite** (a niobate of yttrium and tantalum), **Samarskite** (consisting of the niobates and tantalates of iron, calcium, yttrium, and cerium earths), and **Yttrotantalite** (consisting of niobates and tantalates of yttrium, iron, cerium earths, and uranium). At the present time, however, these minerals are only rarely used as sources of tantalum since the demand for the metal can be fully met by the extraction of tantalite and columbite.

Geographical Distribution of Tantalum Ores.—The most important tantalum-producing areas are the Greenbushes and Pilbara districts of Western Australia; the tin-bearing districts in the Northern territories of South Australia; and South Dakota and Mexico. Of these, Western Australia yields probably the richest ores.

Minor deposits of Ta ores have, however, also been located at various localities in Scandinavia, and in Russia, France, Italy, and Germany (notably in Saxony). These deposits, like occurrences in Nigeria and Ceylon, have acquired importance in the last few years, because of the increasing demand for Ta.

Some typical compositions of tantalum-bearing ores are shown in Table I below. Only the major constituents are recorded there; the difference between the sum of these and 100 per cent. is usually made up of traces TiO_2, WO_3, ZrO_2, MgO, CaO, ThO_2, and SnO_2.

TABLE I

Substance.	Tantalite.*	Columbite.†	Samarskite.‡	Fergusonite.*
Ta_2O_5 - - -	76.34	7.30	13.64	28.50
Nb_2O_5 - - -	7.54	67.35	39.76	29.66
Fe_2O_3 - - -	13.90	2.05	12.15	0.76
FeO - - -	...	9.22	...	...
Y_2O_3, etc. -	...	...	15.80	33.47
Ce_2O_3, etc. - -	...	...	0.70	...
MnO - - -	1.42	10.30	0.42	...
U_3O_8 - - -	...	...	12.09	2.24

* *Min. Ind.*, **17**, 800 (1908). † Col. Rep. Misc. Ser., Cmd. 3190, 30.
‡ *Bull. Imp. Inst.*, **10**, 483 (1913).

Manufacture and Properties of Metallic Tantalum.—Since tantalum minerals are not readily soluble in any of the common mineral acids (except, perhaps, strong hydrofluoric acid), the powdered ore must first be fused with about three times its own weight of caustic soda or potassium bisulphate. The clear melt is then thoroughly leached with water to extract all impurities other than Fe, W, and Si, and the solid residue successively digested with ammonium sulphide and dilute hydrochloric acid (in order to remove W and Fe respectively). Finally, the precipitate is boiled with hydrofluoric acid (whereby Si is vaporised as SiF_4), treated with potassium hydrogen fluoride in quantities sufficient to form the double salts K_2TaF_7 and $(2KF)NbF_3$, and the solution evaporated to dryness. During this last step, the tantalum salt crystallises out preferentially, and this can, if desired, be further purified by fractional recrystallisation.

From potassium fluo-tantalate K_2TaF_7, metallic tantalum is obtained either by electrolysis or by reduction *in vacuo* with sodium metal. Any residual traces of impurities may be removed from the product by melting *in vacuo* between pure tantalum electrodes.

Bars of metallic tantalum are normally produced by compressing the powder and heat-treating it in vacuum furnaces. Such bars can be hammered and rolled or drawn, but these operations must always be carried out at *ordinary* temperatures; at elevated temperatures tantalum combines rapidly with all common gases.

Pure tantalum is a platinum-white metal melting at 2,996° C., and possessing a specific gravity of 16.6. Its hardness depends upon its previous history: tensile strength between 22 and 77 tons per sq. in., and Brinell hardness numbers between 40 and 220 have been reported, and it has also been stated that gas-hardened tantalum may have Brinell numbers of up to 600.

The coefficient of linear expansion of pure tantalum is 7.9×10^{-6} and its specific heat about 0.035 (0.003 over the range -185 to 0° C.; 0.035 at 0° C., and 0.038 at 58° C.).

Chemically, tantalum is unusually inert. It is, for example, unaffected by strong mineral acids and even hot *aqua regia*, and only very superficially attacked by strong superheated solutions of caustic alkalies. In the cold it is only corroded by hydrofluoric acid.

In air it tarnishes slightly, but can be heated to about 600° C. without further change: at higher temperatures (particularly when heated in oxygen) it begins to burn.

Uses of Metallic Tantalum.—Owing to the ductility, hardness, and toughness of the metal, considerable quantities of tantalum are nowadays used in the manufacture of tank and pipe linings and of tubing. The chemical inertness of the metal has also led to its adoption in steam-raising equipment, particularly for the thermal treatment of acids (*e.g.*, hydrochloric acid heaters). Since the rate of heat transfer through tantalum at steam temperatures is unusually high, a tantalum coil is equivalent to a base-metal coil having eighteen times its heating area.

In recent years considerable progress has also been made in fabricating equipment in which tantalum is used as a coating for base metals and increasing quantities of the metal are now being used in the manufacture of certain alloys and temperature-resistant high-speed tools (particularly cutting tools). The alloys contain from 1–40 per cent. Ta combined with varying proportions of molybdenum, tungsten, carbon, nickel, vanadium, and silicon, and it has been reported that tantalum can also replace part or all of the tungsten or molybdenum in these alloys.

For Ta-Mo alloys an extremely high corrosion resistence has been claimed (cf. *Times Rev. Ind.*, July 1950). In corrosion tests in which alloys varying in composition from pure molybdenum to pure tantalum in steps of 10 atomic per cent. were maintained in concentrated aerated H_2SO_4, HCl, and HNO_3 at 50° C. it was found—

(1) that H_2SO_4 only attacked alloys containing more than 50 atomic per cent. of molybdenum (with a maximum corrosion rate of 1 mg./sq. dm./day),
(2) that HCl only attacked alloys containing more than 40 atomic per cent. of molybdenum (with a maximum corrosion rate of 2 mg./sq. dm./day), and
(3) that HNO_3 only attacked alloys containing more than 65–70 atomic per cent. of molybdenum.

Alloys containing iron, tantalum, and niobium have been used to some extent in the manufacture of high-speed steels, but these appear to have no real advantage over the usual tungsten high-speed steels, and are, in any case, considerably more expensive.

Metallic tantalum is now also internationally recognised as a substitute for platinum in the manufacture of precision weights.

In medical practice tantalum has been found very useful in the treatment of war wounds and in trepanning; the metal has no irritating effects upon body tissues, and these will, in consequence, readily adhere to, and grow over, tantalum. As a wire of 0.003 in. diameter, tantalum has also been employed as a replacement for different kinds of nerves.

Finally, it may be noted that tantalum is also used for the construction of spinnerets required in rayon manufacture; for the production of certain surgical and dental instruments; and because of its high sorption capacity, in electrical and radio work. Indeed, although no statistics are available, it looks as if the greater proportion of metallic tantalum currently produced is used for the manufacture of radio valves and power tubes.

Of tantalum **compounds,** only the carbide seems so far to have found industrial uses: cemented with about 8 per cent. nickel, this substance has been used as a substitute for tungsten carbide tools, and it has been claimed that it is even tougher than tungsten carbide.

Estimation of Tantalum and Niobium in Minerals.—The complete analysis of a complex tantalum mineral is often a tedious and complicated undertaking, but the following brief outline of a process for the separation and estimation of tantalum and niobium may be of service.

About 1 g. of the finely ground tantalite is fused for several hours with about five times its weight of potassium bisulphate and, after cooling, the melt is lixiviated with 5 per cent. sulphuric acid. The insoluble matter is separated by filtration and again fused. The sulphuric acid solutions thus obtained are diluted to 200 c.c. and, after nearly neutralising with ammonia, saturated with sulphur dioxide and well boiled for about one hour. This causes the precipitation of any traces of niobium and tantalum which may have passed into solution. The precipitate, together with the insoluble residue previously obtained, will now contain all the niobium, tantalum, silica, together with some of the tin, tungsten, and titanium. The moist precipitate is digested with ammonium sulphide in order to remove the tin and tungsten, and is then washed, transferred to a platinum basin, and dissolved in a few drops of hydrofluoric acid. After diluting the solution to about 20 c.c. it is boiled in order to expel silica. If the quantity of titanium present in the ore does not much exceed 5 per cent., niobium and tantalum in the hydrofluoric acid solution can be separated and estimated by the Marignac process, but if titanium is present in large quantity the separation is ineffective, and some other process must be adopted. The presence of titanium in tantalum ore also causes a large amount of the tantalic and niobic oxides to pass into solution after the fusion with potassium bisulphate, and special methods of analysis have to be adopted (see T. Crook and S. J. Johnstone, *Min. Mag.*, 16, 244, 1912). Assuming that only a small quantity of titanium is present, tantalum and niobium are separated as follows: The solution in very dilute hydrofluoric acid is concentrated to about 20 c.c., heated to boiling, and to it is added a boiling solution containing about 0.7 g. of potassium fluoride. The solution is slowly evaporated to 10 c.c. and let cool slowly to about 15° C. When thoroughly cold, the clear solution, which contains all the niobium and a small part of the tantalum, is decanted through a small filter into a small platinum dish. The residual mass, consisting of crystals of potassium fluotantalate, is washed four times with a few c.c. of cold water, the washings being added to the main solution, which is evaporated to about 5 c.c. and let cool slowly. This solution is decanted and the crystals washed four times with a few c.c. of cold water, and then examined with a lens for flat plates of potassium fluoxy-niobate. If these are present they must be removed by further washing. Next evaporate the solution to dryness on the water bath, cool, add one drop of hydrofluoric acid and 0.1 g. of KF dissolved in 1 c.c. of water. Then run into the dish from 1–5 c.c. of water according to the proportion of niobium expected to be present, allowing 1 c.c. for each 7 per cent. of Nb_2O_5. Heat rapidly for a few seconds, note the total bulk of solution, and set aside to cool for one hour. Filter the solution into a small platinum dish and wash the residue three or four times with a few drops of water, making note of the approximate bulk of the washings. To the solution add 8 c.c. of strong sulphuric acid, evaporate to fuming, and maintain at this temperature for at least twenty minutes in order to remove the last traces of hydrofluoric acid.

After cooling, the solution is poured into 150 c.c. of cold water, and the whole boiled for about twenty minutes in order to completely precipitate the niobium. The solution is filtered and the precipitate well washed with boiling water, dried, ignited, and weighed. The whole of the niobium and a small proportion of the tantalum is contained in this precipitate; the tantalum being allowed for on the following basis: 0.00365 g. Ta_2O_5 for each c.c. of solution from which the final crystallisation took place, and 0.00091 g. Ta_2O_5 for each c.c. of wash water in the final filtration. The remainder of the tantalum is recovered by dissolving the crystallised potassium fluo-tantalate in a few c.c. of water, adding about 10 c.c. of concentrated sulphuric acid, and evaporating to fuming. When cold, the acid solution is poured into about 200 c.c. of water, and the tantalum precipitated by the addition of ammonia. The precipitate is filtered, washed, ignited, and weighed as Ta_2O_5.

A convenient and rapid process for the volumetric estimation of niobium in a mixture of oxides of niobium and tantalum has been described by F. J. Metzger and C. E. Taylor (*Zeits. anorg. Chem.*, 62, 382, 1909). The method depends on the fact that if succinic acid be added to a bisulphate fusion of niobic and tantalic oxides, the solution can be diluted and heated without depositing insoluble compounds of the two elements. When this solution is treated with amalgamated zinc, the niobium is reduced and can be titrated with potassium permanganate. About 0.5 g. of the mixed oxides is fused with 5 g. of potassium bisulphate, 10 c.c. of concentrated sulphuric acid added, and the heating continued until a clear solution is obtained. The solution is poured into a beaker, the crucible rinsed out with 30 c.c. of sulphuric acid, and the whole allowed to cool. Two g. of succinic acid are stirred into the liquid, followed by 20 c.c. of a saturated aqueous solution of succinic acid, and lastly, 200 c.c. of water. The liquid is heated to 75° C., and sent through a Jones zinc reductor (previously warmed by running through it 200 c.c. of 5 per cent. sulphuric acid at 75° C.), filled with 20 per cent. sulphuric acid also heated at 75° C. The niobium solution is followed, first by 50 c.c. of 20 per cent. sulphuric acid, and then by 200 c.c. of 5 per cent. sulphuric acid (both at 75° C.). The brown reduced solution and washings are at once titrated with potassium permanganate in an atmosphere of carbon dioxide. Under these conditions, niobic oxide is reduced to an oxide approximating to the formula $Nb_2O_{3\cdot107}$, whilst tantalic oxide is unaffected.

The degree of amalgamation of the zinc in the reductor is important. It is best prepared by shaking 600 g. of sieved zinc for several minutes with 250 c.c. of a solution containing 0.5 g. of mercury dissolved in 25 c.c. of concentrated nitric acid. The amalgamated zinc is washed first with water and then with dilute sulphuric acid, and is stored under water.

According to a more recent publication, tantalum can also be separated from niobium by precipitation as the iodate. For details of this method (which enables direct estimation of Ta) see T. A. Uspenskaya and Y. A. Charnikov, *Chem. Abstr.*, **35** (2), 440, 1941.

NIOBIUM OR COLUMBIUM

Niobium [1] (Nb; atomic weight 92.91; atomic number 41) is one of a series of comparatively rare elements closely resembling tantalum.

In nature it occurs as the pentoxide Nb_2O_5 in most tantalum ores and in the mineral columbite (which may contain up to 80 per cent. of the pentoxide).

Fairly extensive deposits occur in various localities in the U.S.A. (notably in Connecticut, Maine, and South Dakota) and in Greenland, Norway (near Moss), South Africa, and Madagascar.

For methods of separating niobium from associated metals see the procedures given under "Tantalum."

Metallic niobium may be prepared by reduction of the pentoxide with aluminium, and heating the product *in vacuo* in an electric arc. In this way impurities are removed by vaporisation.

Alternative methods include reduction of the double fluoride K_2NbF_7 with hydrogen; reduction of the pentoxide Nb_2O_5 with calcium in the presence of a small quantity of calcium chloride and an alkali metal; and passage of a mixture of niobium pentachloride and hydrogen through a red-hot tube.

Niobium filaments, which have been used in filament lamps, are made by mixing the pentoxide with paraffin wax, extruding the mixture into the fine threads, and heating these *in vacuo* to 1,900° C.

Metallic niobium is of light grey colour, melts at 1,950° C., and has a specific gravity of 8.4. Its hardness approximates to that of wrought iron.

So far the metal has found only very limited use as a "getter" in vacuum tubes. More recently, however, it has been shown to be a valuable alloying constituent.

Thus, the addition of about 0.5 per cent. Nb to wrought 4–6 per cent. Cr steels reduces air-hardening effects and improves creep- and heat-resistance, and the presence of a similar quantity in stainless austenitic steels prevents grain-boundary precipitation of carbide and consequent corrosion effects (*e.g.*, "weld-decay").

---

[1] In the U.S.A. the metal is known under the name Columbium (Cb); the term niobium is used in Europe.

Another novel application of niobium is in the chromium-aluminium nitriding steels where it effects a large increase in the rate of thickening of the nitrated layer.

Prices.—Current U.S. prices (1949) for ferro-niobium (50–60 per cent. Nb) range between about \$2.25 and \$2.35 f.o.b. plant per lb. of contained Nb.

Estimation of Niobium in Niobium-Chromium Steels.—This is conveniently done by a Cupferron precipitation (*cf.* "titanium"). The relevant details are as follows:—

A 2 gm. sample (5 gm. with niobium contents of less than .5 per cent.) is dissolved in 75 c.c. of 25 per cent. sulphuric acid, cooled, diluted to 100 c.c. with distilled water, and again thoroughly cooled. A little paper pulp is then added with constant stirring and a 6 per cent. solution of Cupferron slowly admitted until the precipitate begins to turn reddish-brown. The mixture is allowed to stand for five minutes, the precipitate filtered off, washed with cold 5 per cent. sulphuric acid containing 1 c.c. of Cupferron solution per litre, and finally thoroughly washed with repeated quantities of cold 5 per cent. ammonium hydroxide solution.

The precipitate and filter paper are then transferred to a platinum crucible, dried and ignited at 650° C. After ignition the residue is cooled, treated with 2 c.c. of 25 per cent. sulphuric acid and 5 c.c. of hydrofluoric acid and evaporated to dryness. It is then fused with 2 gm. of potassium bisulphate, cooled, and extracted with 150 c.c. of a 2 per cent. aqueous HCl solution. The extract is boiled for fifteen minutes, filtered, and the precipitate washed with hot 2 per cent. HCl solution. Finally the precipitate is dried and ignited at 950° C. in a weighed platinum crucible. The proportion of niobium is given by

$$\text{Percentage Nb} = \frac{A}{\text{Wt. of sample taken}} \times 69.90$$

where A = weight of niobic oxide, Nb_2O_5.

It should be noted, however, that this method is not directly applicable to steels containing tantalum, titanium, tungsten, and zirconium unless these constituents are first removed.

REFERENCES

(1) P. Hidnert, "Thermal Expansion of Tantalum." *U.S. Bur. Stand., J. Res.*, Vol. II. (1929).
(2) P. Hidnert and H. S. Krider, "Thermal Expansion of Columbium (Niobium)," *U.S. Bur. Stand., J. Res.*, Vol. XI. (1933).
(3) T. A. Uspenskaya and Y. A. Charnikov, "Separation of Tantalum from Niobium," *Chem. Abstr.*, 35 (2), 440 (1941).

SECTION LXXXI

TUNGSTEN

By Norbert Berkowitz

LITERATURE

L. Gmelin.—Handbuch der Anorganischen Chemie. System No. 54, 1933.
P. Pascal.—" Traité de Chimie Minérale," Vol. XI, 1932.
K. Li and C. Y. Wang.—"Tungsten: its history, geology, ore-dressing, etc." Amer. Chem. Soc., Monograph No. 94, 1943.
J. A. M. van Liempt.—"Separation of Tungsten." Polytechnische School, Delft, 1931.
South Dakota School of Mines.—"Occurrence, Chemistry, Metallurgy, and Uses of Tungsten." Bull. No. 12, 1918.
L. L. Wyman and F. C. Kelley.—"Cemented Tungsten Carbide." Amer. Inst. Min., Tech. Publ. 354, 1930.
B.I.O.S. 820.—Tungsten Carbide in Krupp-Widia Plants.
F.I.A.T. 413.—Tungsten and Molybdenum Wire Manufacture for Use in Lamps and Radio Tubes.
B.I.O.S. 925.—Tungsten Carbide Research in Germany.
B.I.O.S. 962.—Production of Tungsten Wire and Processing of Scheelite.
C. J. Smithells.—"Tungsten." London, 1936.

Until the turn of the century, tungsten (W; atomic weight = 184.0; atomic number = 74) was little more than a scientific curiosity. Since then, however, it has become important as an alloying constituent in the manufacture of hard steels and for the preparation of such materials as electric lamp filaments, and very considerable quantities of the metal are nowadays produced each year.

Natural Occurrence.—Tungsten ores occur generally in veins of older plutonic rocks and are also found in many tin deposits. The most important of these ores are **Wolframite** and **Scheelite.**

Wolframite is a tungstate of iron and manganese, and has the empirical formula $(Fe,Mn)WO_4$. Crystals of wolframite are fairly common; they belong to the monoclinic system and are commonly tabular or prismatic. The specific gravity of wolframite varies between 7.0 and 7.5 and its hardness from 5-5.5. Its colour ranges from dark grey to brown-black, and its lustre is generally sub-metallic. It may also be pointed out that wolframite is sometimes weakly magnetic, and that it forms an intermediate in a series of minerals which ranges from Ferberite, $FeWO_4$, to Hübnerite, $MnWO_4$. The fusion temperature of the series increases with the percentage of hübnerite molecules present in the ore.

Scheelite is a tungstate of calcium, but it should be noted that the scheelite series also includes tungstates of calcium and copper (Cuproscheelite), of copper (Cuprotungstite), of molybdenum and calcium (Powellite), and of lead (Stolzite). Crystallographically scheelite belongs to the tetragonal system. Its colour varies from white or yellowish-white to brown and even reddish, its specific gravity ranges from 5.9–6.1 and its hardness from 4.5–5.0. The composition of scheelite corresponds to 80.6 per cent. WO_3 and 19.4 per cent. CaO. The molybdenum content of the powellite variety may amount to up to 8 per cent.

Geographical Distribution of Tungsten Ores.—The increasing demand for tungsten ore during the last two or three decades has led to large-scale development in so many areas that it is here only possible to indicate the most important deposits.

Wolframite (and its related forms) occurs in substantial deposits in Bohemia (Czechoslovakia), in Roumania, and in various places in Saxony (Germany). In France deposits occur in the Haute Vienne and near St Leonard; in Spain at Sierra Almagrera and near Aquilas; and in Portugal at the foot of the Estrela Mountain range. Workable deposits of the mineral have also been reported from Cornwall (Britain). In the United States deposits are located at Long Hill in Connecticut, in Missouri, in the Black Hills of South Dakota, in Colorado, and in New Mexico and Nevada. In Australia wolframite occurs mainly in the Cassiterite deposits in New South Wales and Queensland.

Scheelite, generally found in pegmatite veins or in ore veins associated with granites or gneisses, is found in Czechoslovakia (particularly in Bohemia); in Germany (in Saxony); in Italy (in the Trantino district and Piedmont); and in Switzerland (near Berne). Small deposits of the crystalline material have been reported from the Vosges Mountains in France, from Lake Ladoga in Finland, and from Cumberland and Cornwall in Great Britain. In America considerable deposits have been located at Long Hill in Connecticut, in Lawrence County in South Dakota, at Leadville in Colorado, and in various localities in Arizona and California.

Cuprotungstite has been found in the copper mines of Santiago in Chile and near Cordoba in Spain; and more recent reports have also indicated the presence of the mineral in workable deposits at various localities in New South Wales (Australia); and in Utah and California (U.S.A.). Powellite occurs in Siberia and in the United States in Idaho, Texas, Utah, California, and Nevada. Stolzite occurs mainly in Bohemia, Sardinia, and at Broken Hill in New South Wales.

Extraction of Tungsten from its Ores.—At the present time it is customary to extract metallic tungsten only from hand-picked wolframite containing some 70–75 per cent. WO_3. A general method of extraction is as follows:—

The raw (and sometimes "dressed") ore is finely crushed and heated in a reverberatory furnace with sodium carbonate; the amount of sodium carbonate added is equivalent to an excess of about 10 per cent. over the amount required to convert all the WO_3 in the ore to sodium tungstate in accordance with the reaction equation:

$$2FeWO_4 + O + 2Na_2CO_3 = 2Na_2WO_4 + Fe_2O_3 + 2CO_2.$$

About 10 per cent. of sodium nitrate is also sometimes added to the mixture, which is maintained at red heat for about four hours. During this time care must be taken that the mass attains a pasty consistency but that it does not fuse. According to G. Erhard (*Metallurgie*, 9, 441, 1912), it is advisable to cool after about four hours' heating and then to recrush the mass in a ball mill and submit it to a second sintering process. The first heating converts about 70 per cent. of the available tungsten into sodium tungstate whilst the second increases this amount to about 90 per cent.

When the conversion is complete, the mass is removed from the furnace, cooled and leached with water in superimposed vats arranged in such a way that the weak liquor from the final washing of one batch is used for the first leaching of the next. The solution thus obtained[1] is then treated with calcium chloride in order to precipitate calcium tungstate. From this, tungstic oxide, WO_3, is prepared by reaction with hydrochloric acid, and this is finally purified by re-dissolving in ammonia, filtering the solution and reprecipitating with mineral acid.

---

[1] The solid residue from this treatment frequently contains cassiterite (tinstone) which can be recovered separately.

The resulting pure WO_3 is then reduced by hydrogen in silica tubes at 1,200° C. to yield grey, amorphous tungsten.

As an alternative, the initial roasting of the ore can be replaced by ball-milling with NaOH in steam-jacketed mills at 80°–90° C. for twenty hours and neutralising the resultant mass with HCl. According to German claims (*cf.* F.I.A.T. Final Report No. 413), this method is suitable for low-grade Wolframite ore.

For Scheelite ore, a somewhat similar extraction has been devised. After ball-milling, the ore is boiled with hydrochloric acid (sp. gr. = 1.143), the product dissolved in ammonia to remove molybdenum, and the clear filtrate precipitated with calcium chloride.

In order to obtain the metal in more workable form, the amorphous powder is normally pressed and sintered at about 1,300° C. in an atmosphere of hydrogen.

It may be pointed out that several alternative reduction processes have been suggested from time to time, for example, reduction with carbon or metallic zinc in an electric furnace; conversion of WO_3 to the nitride followed by heating; and reduction with aluminium or magnesium. Of these methods, however, only reduction with carbon has been used on a large scale, and even this has now been generally abandoned in favour of reduction with hydrogen, which appears to produce a rather purer product.

If **tungsten wire** is required, the sintered bars, obtained as described above, are heated to about 3,200° C. in order to raise the density from about 12 to 19, cooled, and swaged in alloy steel ("Hardmetall") dies so mounted that the two halves of the die exert a hammering action on the tungsten. The resultant wire is then drawn through tungsten carbide and finally diamond dies at relatively low temperatures. Sag-resistance is normally ensured by introducing small quantities (up to .25 per cent.) of alkali silicates into the tungstic oxide before reduction. Metallic tungsten used for these processes must, however, be very pure; in particular it must be entirely free from oxide and from iron, nickel, and non-metallic impurities, such as sulphur and phosphorus. Its carbon content should not exceed about .1 per cent.

Properties of Metallic Tungsten.—Metallic tungsten, as produced by the processes described above, will generally have a purity of, or greater than, 99.75 per cent. It is a steel grey metal, somewhat similar to molybdenum, with a specific gravity of 19.3, a melting point of 3,370° C., and a tensile strength of the order of 200 tons/sq. in. Its coefficient of thermal expansion is low (4.3×10^{-6} over the range 0–100° C., and 4.6×10^{-6} over the range 0–500° C.; Hidnert and Sweeney, 1925).

The electrical resistivity of tungsten is also low, amounting to 5.0 microhms per cu. cm. at 25° C., and increasing to 25.3 at 727° C. and 118 at 3,237° C. (Langmuir, 1916).

Chemically, the metal is extremely inert, being highly resistant towards attack by most mineral acids and oxidising in air only at red heat. It is, however, rapidly attacked by a mixture of concentrated nitric and hydrofluoric acid, and by the vapours of sulphur and phosphorus. Fused nitrates, peroxides, and alkali carbonates and hydroxides also attack the metal.

Tungsten in Industry.—Owing to fluctuating demands for tungsten metal, no precise figures for annual world production of this metal can be given; it may, however, be useful to note that total production of tungsten immediately prior to the second world war amounted to about 22,000 metric tons. Of this total, some 38 per cent. was produced by China, 26 per cent. from the British Commonwealth (mainly from Burma, which was responsible for about 16.5 per cent.), and the remainder mainly from the American Continent (U.S.A. and Bolivia), and from Portugal. Smaller outputs derive from Korea, Indo-China, and Sweden. Production figures for the U.S.S.R. are not available.

To-day, by far the greatest proportion of the output of metallic tungsten is used for the manufacture of tungsten steels; the hardness of these steels increases *pro rata* with the amount of tungsten added up to some 15 per cent., and more slowly thereafter. A common addition for steel hardening consists of about 18 per cent. tungsten, together with about 4 per cent. of chromium and 1 per cent. of vanadium. For special purposes, however, as much as 22 per cent. of tungsten is occasionally used (as, for example, in the manufacture of armour plate and armour-piercing missiles).

Self-hardening steels, *i.e.*, steels requiring no tempering after forging, contain between 2.4 and 3.4 per cent. of tungsten and up to 6 per cent. of chromium. Of particular interest in this connection is "Stellite," a non-rusting alloy containing 5 per cent. tungsten, 20 per cent. copper, and the balance cobalt. This alloy retains great hardness at high temperatures and is therefore particularly suitable for tipping, cutting, and milling tools, and for use in valve-seats, dies, roll-crusher teeth, etc. Stellite was first described by E. Haynes (*Bull. Amer. Inst. Min. Eng.*, 249, 1913), and is protected by U.S. Patents 1,057,423 and 1,057,828 (1913).

A Ni-Cu-W alloy, in which tungsten is the major component, has also been reported. This is made by mixing tungsten powder with a small quantity of nickel and copper powder, about 6 per cent. and 4 per cent. respectively, compressing the mixture and heating to a temperature above the melting point of nickel (1,455° C.). The sintered alloy is stated to have a specific gravity of 16.5 and a correspondingly high absorption coefficient for X-rays. Because of its high density the alloy is also very suitable for use in balancing internal combustion engines and crankshafts.

Smaller quantities of tungsten, usually not exceeding 2–3 per cent. are, moreover, added to copper-tin alloys used in the production of bronzes for decorative purposes.

Minor uses include the adoption of tungsten in anti-cathodes of X-ray tubes, as filaments in modern electric light bulbs, as electrodes for atomic hydrogen welding, in tungsten arc lamps, and in electric contacts in radio valves and magnetos. Because of its low thermal expansion, tungsten wires are also used as in-leads through boro-silicate glasses.

The addition of tungsten up to about 2.5 per cent. has also been reported to improve considerably the heat resistance of nickel-chrome and silicon-chrome valve steels.

A novel application for tungsten has finally been found in the plating industry, where it is used as a plating material on brass and other base metals. The plating has a bright silvery lustre and is, unlike chromium plating, not attacked by the common mineral acids. It has the further advantage that it is also unaffected by sulphur or phosphorus. The plating solution is itself prepared by adding tungsten trioxide, WO_3, to a saturated solution of sodium carbonate at 100° C. until the sodium tungstate formed in the reaction is no longer soluble. The solution is usually electrolysed at 75 amp. per square foot, and it is stated that the brightness of the deposit increases with the temperature of electrolysis. It is, however, important to note that tungsten plating solutions are somewhat unstable and that they will slowly deteriorate through long and continuous use.

Of **tungsten compounds**, only the **carbide** has so far found extensive use. This material is thus the major constituent in a series of alloys used for the construction of lathes, tools, milling cutters, etc.; an example is "Wimet," an alloy at present manufactured by Hard Metal Tools Ltd., Coventry, and containing up to 11 per cent. tungsten carbide and up to 15 per cent. of titanium carbide. It has found particular use in the manufacture of drawing and extrusion dies.

Apart from tungsten carbide, however, some use has been found for tungstic oxide and potassium and sodium tungstates.

Tungstic oxide is used for the production of **magenta bronze**; this is made by adding the oxide to fused potassium carbonate until the solution is saturated, heating the product thus obtained in hydrogen, and then successively treating with water, hydrochloric acid, and potassium hydroxide solution. This process yields a product which has the composition $K_2W_4O_{12}$, and consists of small violet crystals.

An alternative process consists in fusing together the calculated quantities of tungstic oxide and alkali carbonate and then electrolysing the fused mass. Magenta bronze, like certain other alkali tungstate bronzes, is used mainly for decorative purposes and has the advantage that it is insoluble in acids. According to an early article by Philipps (*Ber.*, 15, 499, 1882), the following tungsten sodium bronzes have been prepared: $Na_5W_6O_{18}$, golden yellow; $Na_2W_5O_{15}$, blue; $Na_2W_3O_9$, red; and $Na_4W_5O_{15}$, reddish-yellow. Blue **tungsten-lithium bronzes** have been described as early as 1898 by Hallopeau (*Compt. rend.*, 127, 512, 1898), and later by Knorre and Schäfer (*Ber.*, 35, 3407, 1902). An account of other tungsten bronzes has been given by Engels (*Zeits. anorg. Chem.*, 37, 125, 1903), and by Schäfer (*ibid.*, 38, 148, 1904).

It may also be noted that **sodium para-tungstate** has found a limited application in the textile industry, particularly in fireproofing cloth and other fabrics, and as a mordant for calico printing.

Finally, **tungstic oxide** has been used for the production of yellow glass and porcelain.

Price of Tungsten.—This has been subject to very considerable fluctuation since 1945. In 1946, quotation for wolfram stood between 75s. and 80s. a unit, c.i.f.; by the beginning of 1950 they had increased to about 125s. a unit, and present prices (quoted in London, and greatly influenced by the outbreak of hostilities in Korea) range between 190s. and 200s. per unit (cf. *Times Review of Industry*, 96, September 1950). Latest delivery prices are: tungsten metal powder (98–99 per cent.), 13/6 per lb.; ferro-tungsten (80–85 per cent.), 12s. per lb.

Analysis of Tungsten Ores

Case 1. Tungsten Content greater than 3 per cent.—Digest 2 gm. of the ore with 40 c.c. of hydrochloric acid (sp. gr. 1.16) just below the boiling point until decomposition is completed. Then oxidise the solution by careful addition of nitric acid (sp. gr. 1.42; see note 1), evaporate the solution to a total volume of about 5 c.c., redissolve in 150 c.c. of dilute (1 : 4) hydrochloric acid, boil for a further five minutes and allow to stand. Filter the precipitate on a paper pad, wash with hot 5 per cent. hydrochloric acid, and finally treat with a 2 per cent. ammonium nitrate solution. Then ignite the precipitate in a platinum crucible at a maximum temperature of 800° C. Allow the residue to cool, add 1 c.c. of 25 per cent. sulphuric acid and 2 c.c. of hydrofluoric acid, evaporate to dryness and gradually increase the temperature to 800° C. to complete the ignition. Allow to cool and weigh (A).

Then fuse the residue with 5 gm. of sodium carbonate and extract the cooled melt with 100 c.c. of water. Boil for some minutes, filter, wash with hot water, and set the filtrate aside (see notes 2–4). Dry and ignite the insoluble residue in the platinum crucible, cool and weigh (B).

The percentage of tungsten is then given by

$$\text{Percentage W} = \frac{A - B \times 79.3}{\text{Wt. of sample used}}$$

where A − B is the weight of tungstic oxide.

Notes.—

1. Care should be taken to avoid an excess of nitric acid.
2. With titanium tungsten steels, washing the precipitate with hot water needs to be conducted very carefully as hydrolysed titanium compounds otherwise tend to pass through the filter.

3. With chromium steels, the tungstic oxide residue may be contaminated with chromic oxide. This is determined and corrected for as follows. Acidify the alkaline filtrate with 15 per cent. sulphuric acid, adding 20 c.c. excess. Heat to boiling point, add a 1.2 per cent. $KMnO_4$ solution until a permanent pink colour is observed. Boil for a few minutes, remove excess $KMnO_4$ by adding a little hydrochloric acid, boil for a further ten minutes, cool, and titrate with N/10 ferrous ammonium sulphate and potassium permanganate solution. The percentage of chromic oxide is then equal to the number of c.c. of ferrous ammonium sulphate × 0.002534. Deduct the figure obtained from weight A.
4. If the sample under test is a high speed steel and hence requires the most accurate work, the filtrate should also be examined for the presence of molybdic and vanadic oxides and allowance must be made for these in the weight A. In the determination of these constituents see the analytical procedures given for molybdenum and vanadium respectively.

Case 2. Samples containing less than 3 per cent.—Place 5 gm. of the ore in a 600 c.c. beaker, add 50–75 c.c. of hydrochloric acid (sp. gr. 1.16) and digest near boiling point. When the solution is complete, oxidise with nitric acid (sp. gr. 1.42), but avoid adding excess. Then evaporate to dryness, bake the residue for one hour at 105° C., dissolve in 50 c.c. of 50 per cent. hydrochloric acid, dilute to 300 c.c. with distilled water, heat to boiling and add 5 c.c. of a 10 per cent. solution of cinchonine (see note 1). Boil for one minute and allow to stand overnight.

Filter on a paper pad, wash with 5 per cent. hydrochloric acid containing a little cinchonine solution, and finally with a 2 per cent. ammonium nitrate solution. Transfer the pad and precipitate to a platinum crucible and ignite at 800° C. maximum. Complete the determination as described under Case 1.

To prepare the cinchonine solution dissolve 10 gm. of cinchonine in 50 c.c. of hydrochloric acid (sp. gr. 1.16) and dilute with 50 c.c. of water.

Note.—

1. If cinchonine is not available, the solution is reduced with saturated sulphurous acid and acidified with hydrochloric acid. Then add 25 c.c. of a 1 per cent. aqueous solution of Rhodamine B.

SECTION LXXXII

THE ELECTRIC LAMP INDUSTRY

By Sydney J. Johnstone, B.Sc.
Revised by Wilfrid Francis

LITERATURE

B.S. 161.—Tungsten Filament General Service Lamps. 1940.
B.S. 1270.—Schedule for Electric Discharge Lamps for General Purposes. 1946.
J. de Ment and H. C. Duke.—"Fluorescent Chemicals and their Applications." New York, 1942.
C. J. Smithells.—"Tungsten." London, 1936.
F.I.A.T. 413.—Tungsten and Molybdenum Wire Manufacture for Use in Lamps and Radio Tubes. 1945.
B.I.O.S. 276.—Thorium Metal, Zirconium, and other Special Metals—Special Getters. 1946.
B.I.O.S. 395.—German Fluorescent Lamp Industry. 1946.
B.I.O.S. 33.—The German Electric Lamp Industry. 1946.
"The Mass Production of Osram Fluorescent Lamps." *Osram Bulletin, G.E.C. Progress Sheet*, Vol. 25, No. 2 (1948).
A. G. Perry and C. D. Jones-Thomas.—"Precision in the Manufacture of Osram Incandescent Lamps." *Osram Bulletin* (1948).
H. A. Miller.—"Cold Cathode Fluorescent Lighting." London, 1949.

The modern electric lamp may be described briefly as consisting of a glass bulb, enclosing a fine thread of some refractory substance, known as the filament, which, when heated by the passage of an electric current, will radiate light. The atmosphere in the bulb is either reduced nearly to a vacuum, or an inert gas, such as nitrogen or argon, is used.

The numerous problems involved in the manufacture of the various types of electric lamps are mostly of a mechanical, rather than a chemical nature, and, therefore, cannot be fully discussed in this volume. Metal filament lamps have almost entirely displaced the carbon filament variety which was the first practical electric lamp.

Carbon filament lamps are usually evacuated so as to leave a pressure of about 0.005 mm. in the bulb.

HISTORICAL

Carbon Filaments.—In the earlier types of lamp these were made of carbonised bamboo or cotton fibre, but they were later made from cotton wool, which was dissolved in a strong solution of zinc chloride to give a thick syrupy liquid. This dark greenish solution was squirted by pressure, through various-sized nozzles, which were immersed in jars of methylated spirit. As the solution was forced from the jet, the cellulose was precipitated by the methylated spirit, and so formed a continuous filament.

The gelatinous filaments, thus produced, were removed from the solution and air-dried on frames. When dry, the filaments, which then resembled cat-gut, after being examined for defects, were passed repeatedly through drawplates until they were reduced to the requisite standard diameter. The filaments were next wound on porcelain or metal frames, which had the same shape as was desired for the finished filament, immersed in graphite contained in a crucible, and raised to about 2,000° C. This latter process, which is known as "**metallising**," was sometimes repeated after the filament had been "flashed." By this means a filament of pure carbon of the desired shape was obtained, and after being carefully sorted, the selected filaments were submitted to the process of "**flashing**." This consists in electrically heating the filament to bright redness in a glass jar, having in it an atmosphere of a volatile hydrocarbon, such as ligroin or benzene, until it has attained a certain resistance, when the heating current is automatically cut off. The operation was usually conducted by considerably reducing the pressure of air within the jar and then admitting a definite volume of the hydrocarbon vapour. It was usual to employ a current about twice as great as that which will be used in the finished lamp.

Metallic Filament Lamps

There are probably few articles in commerce whose introduction created such widespread interest and demand as the metal filament electric lamp.

Briefly summarised, the transition from the carbon filament to the metal filament lamp was as follows: The carbon filament lamp, with an efficiency of 3 watts per candle power, was succeeded in turn by the "metallised" carbon filament having an efficiency of 2.5 watts, the tantalum with 1.7 watts, squirted tungsten requiring 1.25 watts, and the ductile or drawn tungsten lamp consuming 1 watt per candle power. More recently, however, the nitrogen-filled drawn tungsten lamp has been introduced, and has an efficiency of 0.5 watt per candle power.

The carbon filament lamp, in its many forms, had reigned unchallenged for many years when the first metallic filament lamp was made by Welsbach in 1898, as the outcome of his investigations on the use of metals having a high melting point as incandescent electric illuminants. It is rather interesting to note that the man who, by his invention of the incandescent mantle, put coal-gas lighting on a competitive basis with electricity, should indicate the lines of development for the electric lamp, so that it might equal incandescent gas lighting in efficiency. The changes during the past ten years in the method of manufacture of metal filament electric lamps have been many and varied, and it is not possible to give here a full account of these. The following summary is, therefore, only intended to indicate briefly the more important stages through which the metal filament has passed in order to attain its present degree of efficiency.

In order that a metal may be suitable for use as a filament for incandescent electric lamps, it is essential that it should have a high melting point, be fairly ductile, and possess a low vapour tension under working conditions, whilst its radiation must be highly selective. It has been shown by C. W. Waidner and G. K. Burgess (*U.S. Bureau Standards*, **2**, 319, 1907) that the light emitted by an incandescent metal varies as the twelfth power of the temperature, whilst the energy required varies as the fifth power of the temperature. It is seen, therefore, that a small increase in the working temperature of the filament is of considerable advantage.

The melting points of some of the metals which have been suggested or used as filaments are shown in the following table:—

Tantalum	2,910° C.	Molybdenum	2,650° C.
Thorium	over 1,700° C.	Zirconium	1,850° C.
Tungsten	3,370° C.	Titanium	1,795° C.
Osmium	2,700° C.	Niobium	1,950° C.

Amongst the advantages possessed by metal filaments over those of carbon is that, being good conductors of electricity, their resistance increases with temperature, whereas with carbon filaments increase of temperature causes a decrease of resistance, as the substance is a poor conductor of electricity. For this reason, fluctuations in voltage cause smaller alterations in the intensity of the light given by a metal filament than would be the case if a carbon filament were employed.

The first metal filament lamp constructed on modern lines was one introduced by Welsbach in 1898, the filament of which was composed of metallic osmium, one of the platinum group of metals.

This lamp had many disadvantages besides the high price of the metal, which was at that time about £100 per lb. The lamps had to be burned in a vertical position, otherwise the filaments sagged and broke, and they could not withstand shock. Low voltage lamps only could be produced, and therefore on the ordinary circuit several lamps had to be run in series. The filaments were first made by heating a platinum wire in an atmosphere containing a volatile osmium compound. This caused the deposition of metallic osmium on the wire from which the platinum was subsequently volatilised by increasing the temperature. At a later date, filaments were also made by the "squirting" process, and a lamp having a filament of metallic osmium was on the market, for a short time, under the name of the "**Osmi**" lamp.

After Welsbach had thus indicated the direction in which improved efficiency of the incandescent electric lamp was to be sought, there were numerous attempts to utilise, as filaments, other metals of the platinum group, either alone or alloyed with base metals, in order to reduce the tendency towards volatilisation. After numerous trials, however, the metals found to be most suitable were tantalum and tungsten, neither of which is a member of the platinum group. At the outset, considerable difficulty was experienced in producing filaments of sufficient strength and thinness, and it was soon realised that the filament drawn from a rod of ductile metal had many advantages over one made by the squirting process.

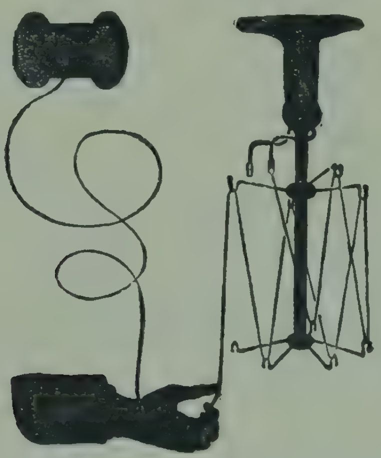


FIG. 1. "Spider."

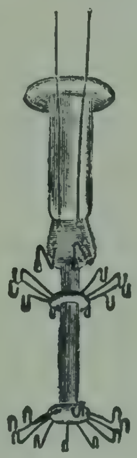


FIG. 2.—Method of Arranging Continuous Filament on "Spider."

The Tantalum Lamp.—The first lamp placed on the market having a filament of drawn wire was the tantalum lamp, which was introduced in 1903 by the Siemens & Halske A.G. of Charlottenberg, Germany. The earlier tantalum lamps had filaments varying in diameter up to 0.28 mm., but with the improvement in the method of making the metal more ductile, it was found possible to make wire having a diameter of less than 0.02 mm. This improvement permitted the production of lamps suitable for use on a current of any voltage commonly employed, but led to a difficulty in accommodating a long length of wire within a bulb of such a size as would be practicable to use. As tantalum has a much lower specific resistance than carbon, tantalum filaments have to be two and a half times the length and one quarter the diameter of carbon filaments for equal voltage and candle power. Thus, a tantalum filament for a 110 volt, 25 candle power lamp is 645 mm. long and 0.047 mm. in diameter, whilst a carbon filament for a lamp of similar voltage and candle power would be about 250 mm. long and 0.18 mm. in diameter. The fact that the working temperature of the tantalum filament was very near to its softening point precluded the use of the double loop sometimes employed in carbon filament lamps, but this difficulty was surmounted by the invention of the "Spider" shown in Fig. 1 (German Patent, 153,328). The method of arranging the filament in zigzag fashion on the spider, as shown in Fig. 2, permits the lamp to be burned in any position.

Tantalum lamps have an initial efficiency of about 1.5 watts per (Hefner) candle power, the light intensity increasing slightly during the first fifty hours of use, and then decreasing slowly (see Fig. 3). The consumption of current per candle power slowly increases with the time that the lamp has been in use (see Fig. 4). The light intensity of the tantalum lamp varies by about 4 per cent. for each 1 per cent. difference in voltage at the lamp terminals. The variations in candle power caused by alterations in the voltage are shown in Table I.

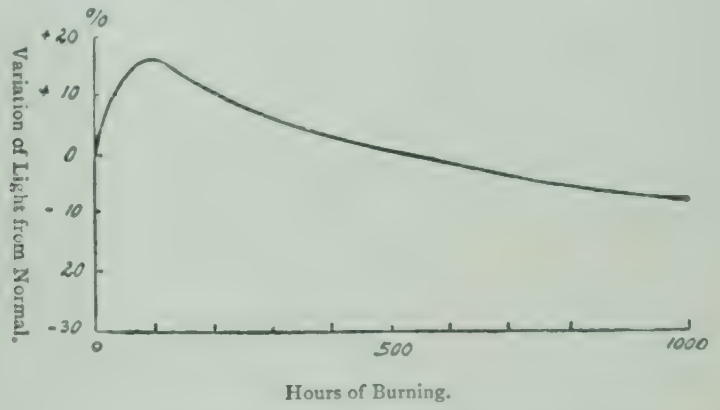


FIG. 3.—Variation of Luminosity of the Tantalum Lamp.

The initial increase in the light intensity may be due to a structural change in the filament, which causes a decrease in its resistance. When examined under the microscope, a tantalum filament, which has been burnt for some time on a direct current circuit, shows a tendency to contract into drops (see Fig. 5). The alternating current, under similar circumstances, causes a disconnected appearance in the filament (see Fig. 6). As would be expected from these observations, tantalum lamps when used on alternating current circuits have a somewhat shorter life than when a direct current is employed.

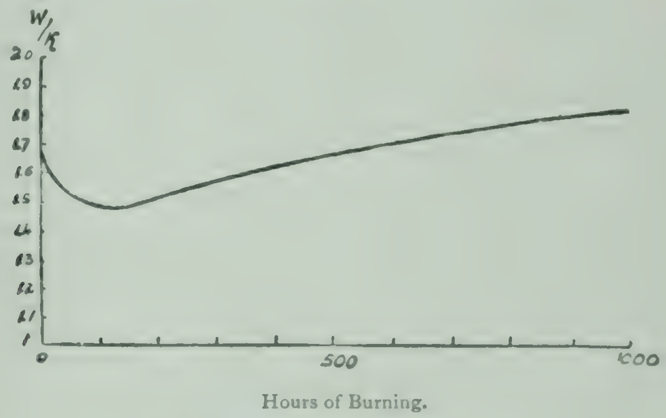


FIG. 4.—Variation in Consumption of Current of Tantalum Lamp.

The tantalum lamp met with great success during its early days, about 103 million lamps being sold during the years 1905–1911, but has now been almost entirely replaced by the tungsten lamp.

The Tungsten Lamp.—The drawn wire tantalum lamp was followed by numerous patents for utilising metallic tungsten as a filament. Owing to the hardness and brittle character of the metallic tungsten produced at that time, the process of making filaments by drawing the metal, in the same way as tantalum was drawn, could not be employed. The filaments, therefore, had to be produced by a "squirting" process, similar to that employed in the manufacture of carbon filaments, or by producing a coating of tungsten on a core of carbon or other refractory substance.

TABLE I

Variation in Pressure. Per Cent.		Candle Power.					Average Candle Power as Per Cent. of Normal.	Watts per Hefner[1] Candle Power.
Below normal	− 20	3.9	6.3	9.9	12.6	19.7	39.4	2.60
	− 15	5.0	8.0	12.5	16.0	25.0	50.0	2.25
	− 10	6.5	10.3	16.1	20.6	32.2	64.5	1.95
	− 5	8.1	13.0	20.3	26.0	40.5	81.0	1.70
Above normal	+ 5	12.2	19.5	30.5	39.0	60.9	121.9	1.35
	+ 10	14.7	23.6	36.8	47.2	73.6	147.2	1.20
	+ 15	17.5	28.1	43.8	56.2	87.7	175.5	1.10
	+ 20	20.7	33.2	51.8	66.4	103.8	207.5	1.00
Normal pressure	...	10	16	25	32	50	100	1.50

[1] The Hefner candle power is equal to about 0.9 British standard candle.

The many processes which have been employed up to the present day may be roughly classified into those involving—(1) Substitution. (2) Amalgamation. (3) Squirting a paste containing tungsten powder. (4) Squirting colloidal tungsten. (5) Drawn wire. (6) Alloy processes.

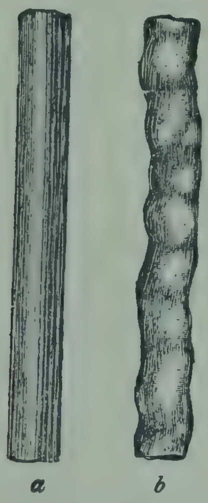


FIG. 5.—Tantalum Filament (*a*) before and (*b*) after Use on Direct Current Circuit.

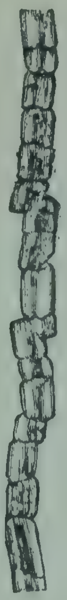


FIG. 6.—Tantalum Filament after Use on Alternating Current Circuit.

In the first-mentioned method, metallic tungsten powder was mixed with an organic binding material, such as gum, and squirted into filaments. The carbon was eliminated by placing the filaments in an atmosphere containing a volatile compound of tungsten, such as the oxychloride, and a small quantity of hydrogen.

When the filament is heated to redness by the passage of an electric current, tungsten is substituted for carbon.

A typical example of the second class of process is one patented by the General Electric Company of the United States. The method consists in mixing metallic tungsten powder with an amalgam containing equal amounts of cadmium and mercury, and squirting the mixture through a die in the usual way. The cadmium and mercury in the filament, thus produced, are subsequently volatilised by heat, and the filament remaining has the usual brittleness, but it is claimed that after moderate heating it becomes pliable and can be bent to any desired shape.

In the third type of process, as in the other classes, numerous modifications have been employed. Thus, the binder may be one which, on heating, leaves a carbonaceous residue, *e.g.*, gum, sugar, gelatine, or nitro-cellulose, dissolved in amyl acetate. On the other hand, it may consist of some substance which, although acting as a binding agent at ordinary temperatures, is volatilised, on heating, without carbonising. Examples of this class of binder are paraffin wax, camphor, and pinene hydrochloride. Binders of this class are employed in the paste process patented by Just, in which filaments are made by mixing a noncarbonising binding agent with a compound of tungsten which is reducible by hydrogen. After pressing and drying, the filaments are reduced in hydrogen at such a temperature that the binder is volatilised. The process avoids the difficulty experienced in completely removing the carbon which is deposited when the other class of binder is used.

Colloidal Tungsten Filaments.—One of the most successful of the squirting paste processes is that in which colloidal tungsten is employed. The feature of the process is that, owing to the plastic and coherent nature of the material, no binding material is required; a much stronger filament being thus produced, and the difficulty of removing the carbon from the filament is avoided.

Colloidal tungsten may be prepared by allowing an electric arc to play between roughened electrodes of tungsten under water, or by the methods of Wedekind or Wright. The finely divided colloidal tungsten can be separated from the water by slow evaporation, and the plastic mass, thus obtained, is squirted into filaments. At ordinary temperatures the filaments, thus obtained, do not conduct electricity at low voltages, but when heated to 60° C. they conduct sufficiently well to enable the final drying and sintering of the filament to be carried out. The preliminary heating to 60° C. can be dispensed with if a current of 400–1,000 volts be used for performing the operation (English Patent 12,968, of 1908). In order to avoid small cavities in the filament, the heating is carried out in a non-oxidising atmosphere, the pressure of which is reduced to at least 150 mm., and preferably to 40 mm. During the operation a continuous current of gas, consisting of about 80 per cent. nitrogen and 20 per cent. hydrogen, is passed through the apparatus. As the temperature is gradually increased the tungsten returns to its massive state, and the filament decreases considerably in size and resistance.

Colloidal tungsten filaments have been produced in large quantities, but this process and the other processes mentioned above are now almost entirely replaced by the drawn wire process.

MODERN DEVELOPMENTS

Drawn Wire Tungsten Filaments.—The manufacture of drawn filaments from metallic tantalum has already been mentioned. The production of drawn tungsten filaments was rendered possible by the discovery of a method of producing ductile tungsten introduced by the General Electric Company of the United States. The general principles involved in the method have been already mentioned in the section on tungsten and the following is an account of the essential details of the process as used in the electric lamp industry.

Pure metallic tungsten is very fragile at forging temperature, but at a white heat it can be hammered, rolled, or drawn, and so be rendered malleable. In order to obtain the metal in this condition, it must be free from oxide, iron, nickel, and contain only traces of sulphur, phosphorus, antimony, arsenic, selenium, or tellurium, whilst the carbon content must not exceed 0.05 per cent. The heating must be performed very gradually, and it is necessary to protect the metal from contact with air during the various stages of its manufacture. The operations may be roughly divided into six sections.

1. *The Production of Pure Metallic Tungsten.*—This is effected by heating pure tungstic oxide in a current of pure hydrogen at a temperature of about 1,000° C.

2. *Agglomeration of the Tungsten Powder into Bars.*—This is effected by means of a hydraulic press, exerting a pressure of about 5,000 kilos per square centimetre (see Fig. 7). The bars, which are about 130 mm. long and 4 mm. thick, are exceedingly fragile, and their formation requires considerable skill. The powder used in this process should be of medium fineness; if it is too fine or too coarse, the bars readily crumble after compression.

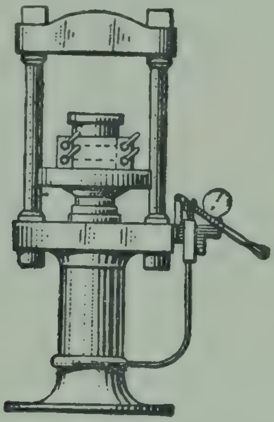


FIG. 7.—Hydraulic Press and Mould.

3. *Consolidation of the Compressed Bars.*—The bar, as it leaves the hydraulic press, is very fragile, and will break if laid on an uneven surface. It is given the desired firmness by heating for about one hour in a current of hydrogen in a tubular furnace, the temperature being slowly increased to full redness. The temperature is then very slowly raised to slightly above 1,000° C.

4. *The Sintering of the Bars.*—The sintering process is intended to create an intimate union between the minute crystals of tungsten, of which the bar is now composed. The operation must be carried out slowly and cautiously, as the quality of the filaments depends largely upon the success of this operation. The bars are heated to a temperature of about 2,850° C. (near the melting point of tungsten) in a special furnace shown in Fig. 8.

The casing of the furnace, which is of cast iron coated inside with graphite, is provided with small tubes *l* and *m* for the admission and discharge of hydrogen. The wall *a* of the furnace is removable, and is normally attached with screws and wing nuts. The opposite wall has two windows *b* and *c*, which permit the operation to be watched. The copper electrodes *d* and *e* are water cooled, the lower one being fixed whilst the upper one is suspended by a counterpoise and carries a bell *o*, which is immersed in a cylinder *k* filled with mercury. The bar to be treated is attached to the electrodes by spring grips, the furnace closed, filled with hydrogen and, as soon as all oxygen is removed, the heating current is turned on. The contraction of the bar during this heating amounts to about 14 per cent. In order to obtain a temperature of 2,650° C. a current of about 53 amperes per square millimetre is required for bars having a cross-sectional area of 16–20 sq. mm., whilst 57 amperes are required for a temperature of 2,730° C. with bars of similar size.

5. *Working the Bars by Hammering and Rolling.*—The sintered bars, as obtained by the last process, are still brittle enough to break if dropped from a height of 30–40 cm., and now require to be worked at a temperature of 1,200°–1,300° C., but as they oxidise very rapidly in air at this temperature, it is necessary to carry out the hammering or rolling, as far as it is possible, in a current of hydrogen. The machine used for this purpose is illustrated in Figs. 9, 10, and 11.

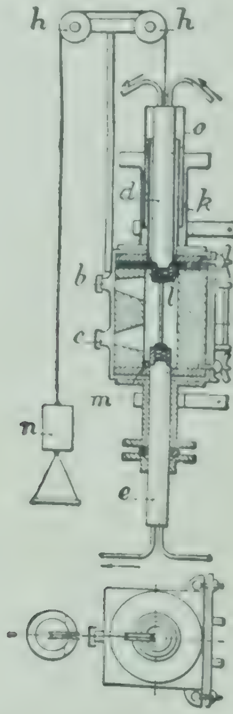


FIG. 8.—Electric Furnace.

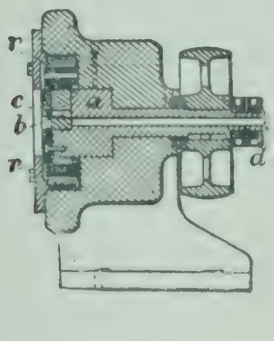


FIG. 9.—Section on A.B.

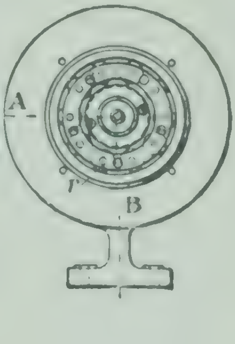


FIG. 10.—View with Cover Removed.

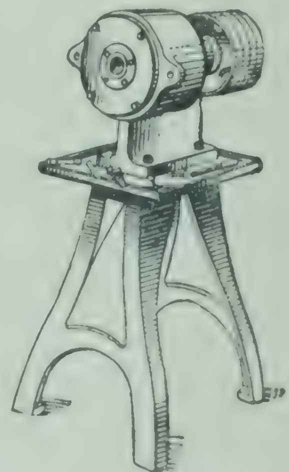


FIG. 11.—Complete Machine.

The dies *b* have on their interior surface a tapering groove of the same size as the bar; they are mounted with the hammer *c* in a recess in the hollow shaft *a*. The hammers, which have rounded external ends, are carried by the rotation of the shaft in front of the rollers *r*, which are arranged in a ring. The rapid revolution of the shaft causes the hammers to be driven outwards by centrifugal force, but they are thrown inwards as they come into contact with each roller and transmit the blows to the dies. When the shaft is rotating at about 400 revs. per minute, the hammers give about 4,000 blows per minute, and these are distributed regularly over the surface of the bar. The latter, after being heated to 1,300° C. in an atmosphere of hydrogen, is quickly thrust into the machine, whilst a continuous supply of hydrogen is led in at *d* in order to prevent oxidation of the metal during the hammering. The diameter of the bar can be reduced about 4 per cent. at each treatment in the machine, so that in order to obtain a wire 1 mm. in diameter from a bar 6 mm. square about fifty treatments are necessary. Every third time that the bar passes through the machine the dies are replaced by others having a smaller diameter. When the wire has been reduced to a diameter of 0.75 mm. the metal has become so ductile that it can be bent and worked at ordinary temperatures.

6. *Drawing the Bars into Wire.*—Although the drawing might be performed at ordinary temperatures, the operation is considerably facilitated by heating the drawplate, the arrangement used being shown in Fig. 12.

The drawplate *a* consists of a cylindrical block in which the diamond is fixed in the usual way. Lighting gas is brought by the pipe *c* to a burner *e*, which is arranged so as to direct its flames upon the periphery of the plate. Before entering the die, the wire passes through a cylindrical tube, which is also heated. The draw tongs *b* are similar to those usually employed in the drawing of steel wire.

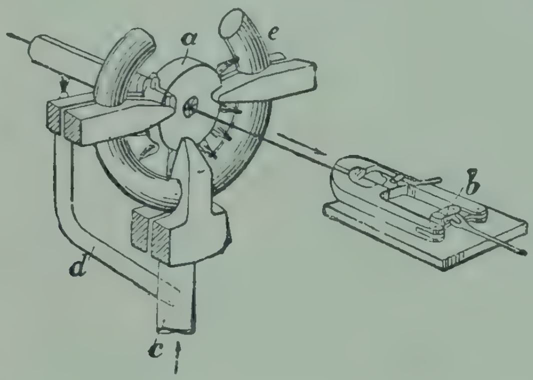


FIG. 12.—Heated Drawplate.

The drawplate is lubricated with a mixture of deflocculated graphite and water. In order to point the ends of the wires, so as to enable them to enter the die, they are either plunged into melted potassium nitrate or, if they are already thin, they are immersed in a solution of potassium cyanide and made the anodes of an electric circuit. The successive dies employed differ very little in diameter, thus, starting with a wire, 0.65 mm. diameter, they decrease by about 0.0125 mm. as far as 0.35 mm., and from this size to 0.1 mm. the interval is 0.0065 mm. From 0.1–0.075 mm. it is 0.03 mm. From 0.075–0.0375 mm. it is 0.0025 mm., and finally from 0.0375–0.025 mm., and below it becomes 0.00125 mm. Thus about 100 dies are necessary. During the reducing of the wire from 0.65–0.45 mm. the temperature is maintained at 600°–650° C., whilst from 0.45–0.25 mm. it is 500° C., whilst for smaller diameters a temperature of about 400° C. is used. The wire thus obtained is coloured blue-black by graphite and a small amount of oxide, and is cleaned by being electrically heated to a dull red whilst passing it through a glass tube containing hydrogen.

Coils of wire are made from the filaments so produced, the diameter of the filament varying with the rating of the lamp. Thus, a 15 watt lamp filament has a diameter of .015 mm., whilst a 60 watt lamp has a filament of .030 mm. diameter. The coils are wound in continuous lengths on automatic machines, the diameter of the coils varying from about three to seven times that of the wire. The mandrels used are themselves manufactured by drawing through diamond dies so as to ensure accuracy in diameter.

The Manufacture of the Lamp.—The bulb is blown in automatic machines from a lime-soda glass with a short working range of temperature. The support for the tungsten filament is made up of the three essential parts:

(1) Support wires of molybdenum;
(2) Lead-in wires of nickel-iron alloy, copper plated;
(3) "Pinch" and rod support, made of lead glass.

In addition, a small glass tube passes through the pinch to allow the bulb to be exhausted after assembly. Lead glass is used for these parts since it has a similar coefficient of expansion to that of the lead-in wires, whilst it is free from the defect of soda glass of conducting electrolytically when hot and releasing sodium. Particular care must be taken in the composition and annealing of the molybdenum wire used for the filament supports, so as to have the correct degree of resilience to enable automatic machines to form loops of the right dimensions without unduly stressing the metal. The annealing of the metal is controlled by tensile strength and elongation measurements. The copper-plated lead-in wire is also made to a close specification to ensure uniform performance. A film of a flux, usually potassium borate, is placed on the lead-in wires before assembly so as to allow the glass of the "pinch," when melted, to wet the metal and make a good seal.

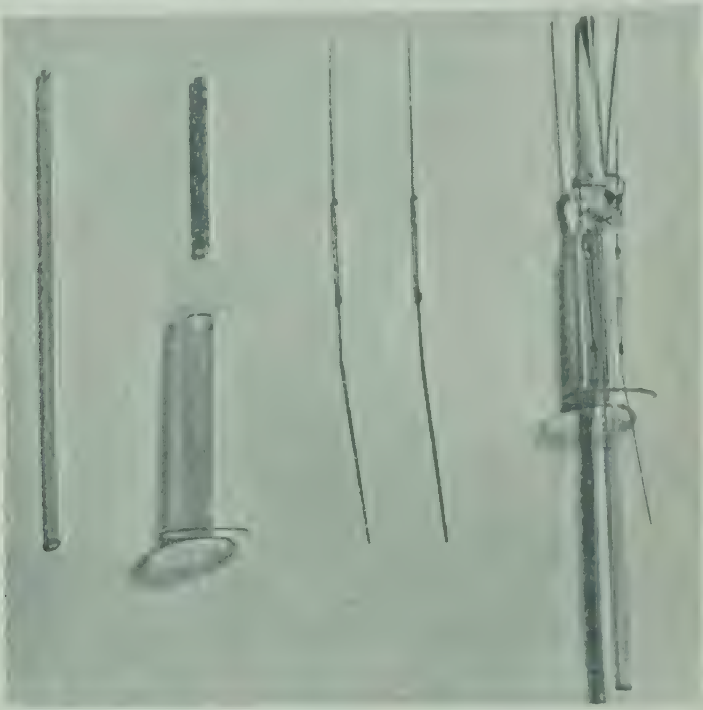


FIG. 13.—Filament Components and Method of Assembly.
(*Courtesy G.E.C. Ltd.*)

The three components of the filament support are assembled by placing in position and sealing by heating and squeezing together the glass tube forming the "pinch" and lead in wires, glass rod, and exhaust tube. These components, and the method of assembly, are illustrated in Fig. 13.

The filament is then placed in position on the molybdenum support wires and the filament assembly placed inside the glass bulb and sealed around the base of the lead-in tube. These operations are illustrated in Figs. 14 and 15a. The subsequent treatment then depends upon whether a vacuum lamp or a gas-filled lamp is being manufactured.

Vacuum Lamps.—The vacuum necessary to be maintained in vacuum lamps is of the order of .0001 mm. of mercury. It is impractical to exhaust to the pressure by the methods of mass production, and, in addition, small quantities of harmful gases, particularly oxygen, carbon dioxide and water, are strongly adsorbed on the glass surfaces and are only released slowly during the application of heat and vacuum. If the pressure in the lamp is in excess of about .005 mm. of mercury, particularly if the residual gas is mainly water vapour, harmful electrical discharges result and the life of the lamp is reduced. Consequently, a method other than protracted evacuation is used to remove the last traces of injurious gases, namely the use of a **getter**. A getter is a compound, that can be applied to the filament before assembly, containing a substance capable of being volatilised on to the inner surface of the glass bulb by heat, and, when there, retaining minute quantities of gases occluded in the glass by processes of chemi-sorption. One getter in general use is a mixture of red phosphorus and cryolite in a liquid binder. The complete process of evacuating the lamp and "cleaning-up" is carried out in two stages. First a number of lamps are assembled on a rotating table and connected to vacuum pumps, whilst the bulbs are heated to about 400° C. When the vacuum has reached the desired limit, usually below .005 mm. Hg, the exhaust tubes are sealed and the filaments heated, in stages, by passing electricity through via the lead-in wires.

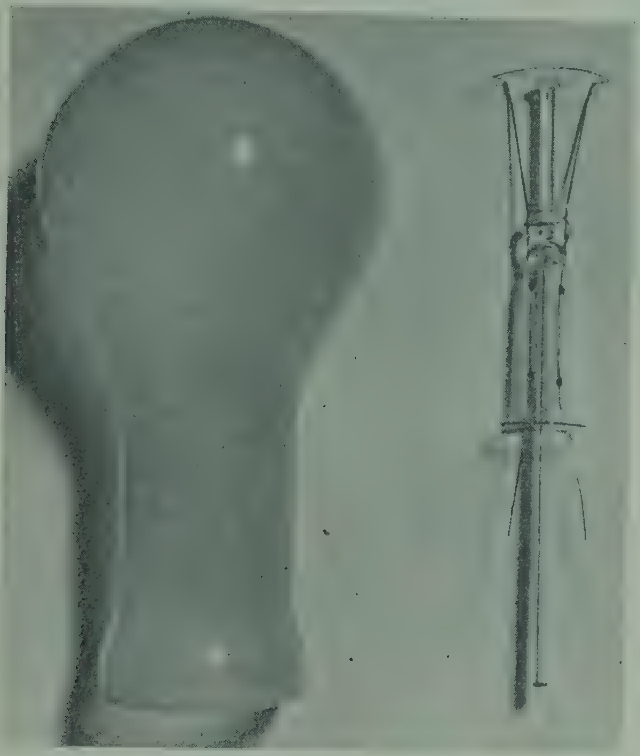


FIG. 14.—Complete Filament Assembly and Bulb.
(Courtesy G.E.C. Ltd.)

The filament is at first heated to a relatively low temperature by the application of about 90 per cent. of its rated voltage, so as to volatilise the phosphorus, and afterwards, for a short time, to a higher temperature than normal by the application of about 110 per cent. of its rated voltage. The layer of red phosphorus on the bulb surface is subjected to a fierce electronic bombardment, which converts it into yellow phosphorus. This vaporises and condenses again as red phosphorus, adsorbing residual gases in the bulb that have been released from the glass. The process continues until all the gas molecules have been chemi-sorbed, or fixed, on the layers of red phosphorus on the glass surface. Since the temperature of the bulb in practice is lower than that during the "cleaning up" process, no gas is released during the working life of the bulb. In most works a proportion of each batch of bulbs is held back and retested seven to ten days after manufacture, so as to make sure that gases have not been released and that the sealing of the lead in wires is effective. After cleaning up, the bulbs are "capped" by placing in thin brass shells, each containing two contacts, pouring in liquid black glass, and pressing into shape. The sealed lamps, before and after "capping," are illustrated in Fig. 15.

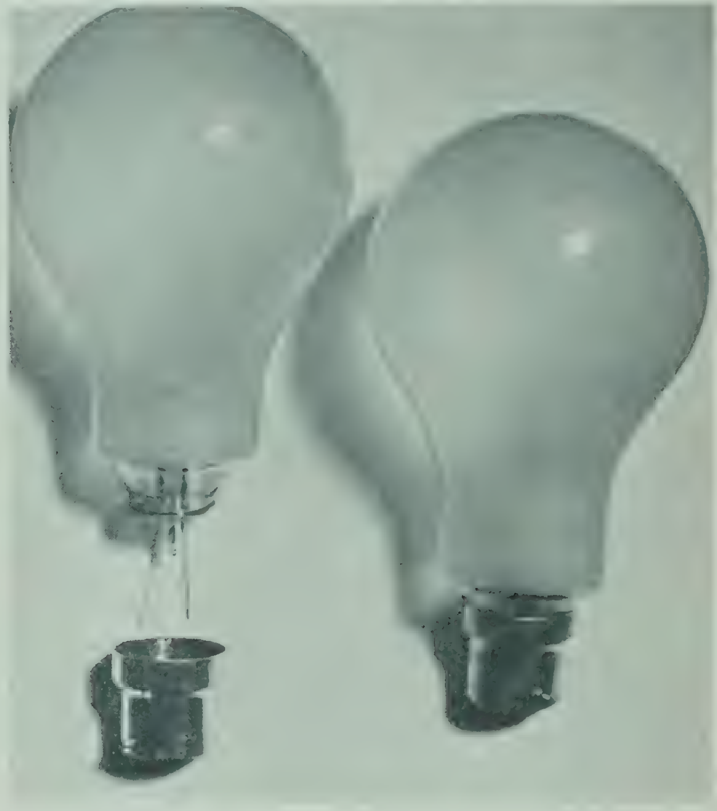

(*a*) (*b*)

FIG. 15.—Lamp Assembled, Evacuated and Capped.
(*Courtesy G.E.C. Ltd.*)

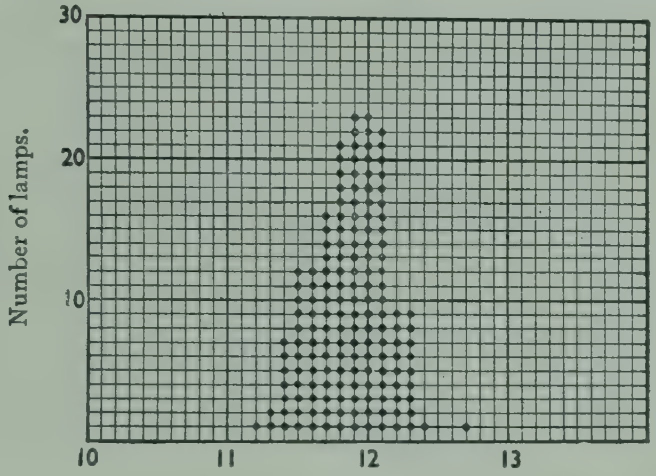
Gas-filled Lamps.—The "cleaning up" method of evacuation, described above, is not applicable to gas-filled lamps because of the presence of the gas, though a getter may still be applied to the filament to help to remove traces of residual oxygen. Instead, evacuation whilst the glass bulbs are hot is very thorough, and the bulbs are swept out with clean, dry nitrogen. They are then filled with a carefully prepared mixture of nitrogen and argon, from which all traces of moisture, oxygen, and carbon dioxide have been removed by chemical or physical means. With both types of lamp, control tests are made regularly for rating, efficiency, and longevity.

Other tests generally applied are B.S. tests for the twist strength of the cap and the electrical resistance of the insulation of the cap. The twist strength should be at least 25 lb. in. and the insulation resistance at least 50 megohms.

Lamp Ratings and Efficiencies.—Lamps are rated in terms of power consumption, measured in watts, and are classified according to voltage. The usual range of power consumption for domestic and industrial metal filament lamps is from about 15 watts to 1,500 watts. The light emitted by an electric lamp is now usually measured in "lumens" rather than in candle power; one lumen being approximately equal to .08 candle power. The efficiency of a lamp is usually expressed in terms of lumens per watt, and a good average figure for a tungsten filament lamp is 12 lumens per watt.

Almost equally important in manufacture is the standard of uniformity attained. Some typical results for Osram lamps, manufactured by the General Electric Company, during the war years 1942–43, are shown in Fig. 16. From this it will be seen that 73 per cent. of the lamps tested lie within ± 2½ per cent. of their average efficiency and 87 per cent. within ± 5 per cent. Fig. 17 shows the effect of small changes in filament diameter on the operational efficiency of the lamp at rated voltage. Although there are five sources of error indicated, any one of which could give rise to an error of 3 per cent. in efficiency, the measured efficiency of the lamps shows that in 70 per cent. the accumulated effect of five possible sources of error is less than 3 per cent.

Fluorescent Lighting.—This popular and efficient form of lighting is rapidly replacing metal filament lamps for all public lighting and for much industrial lighting on account of its high efficiency and low running costs.



Lumens per watt at rated volts.
FIG. 16.—Spread in Efficiency of a typical batch of Osram Lamps.

Cold Cathode Tubes.—The tubes consist of lengths of glass tube with a metal electrode attached to each end. They are filled with neon or argon at a pressure of about 10 mm. Hg. When the necessary voltage is applied, a current passes through the ionised gas, which glows and radiates light. A.C. is used, the electrodes being alternatively positive and negative. The discharge appears continuous owing to the persistance of vision of the eye, but the light has a stroboscopic effect, which is trying visually and may be dangerous in the presence of rotating machinery, since this does not appear to be revolving when the rate of rotation is the same as the frequency of the alternating current. In the early types of neon lighting, high tension current was necessary, the voltage varying from 5,000–15,000, and the current from 15–50 mA. The tubes may be up to 60 ft. long and the normal colour of the discharge is orange red. Additions of other elements, such as argon, mercury, or sodium, modify the colour of the discharge. The efficiency of the neon tube varies from 8–15 lumens per watt. This is similar to that of the tungsten filament lamp. In large rooms it is an advantage to instal three tubes, one operated from each phase of a three-phase supply, so as to reduce the stroboscopic effect. Luminescent materials are sometimes used for coating the inside of the tubes and are applied as a thin cream in a solution of nitro-cellulose, which acts as a binder for the powders. These fluoresce in the presence of the ultra-violet light, also present in the low-pressure discharge. Variations in the composition of the powders, or of the inert gas used, enable different coloured effects to be obtained, or the "daylight" effect which is often required. The cellulose nitrate film is decomposed by passing the tubes through a gas-fired furnace, leaving a thin, dry coating of powder adhering to the tubes.

Hot Cathode Tubes.—Ordinary 200–400 volts will operate the recently developed hot cathode tubes. With these, higher current densities are possible, with correspondingly increased output of light at increased efficiency. The electrodes consist of a cathode, consisting of a tungsten coiled-coil filament, and an anode which, according to the lamp rating, either takes the form of a pair of metal plates attached to the leading-in wires, or is an integral part of these wires. After assembling the electrode components, the cathodes are coated with electron-emitting materials, consisting of a mixture of barium and strontium carbonates in a

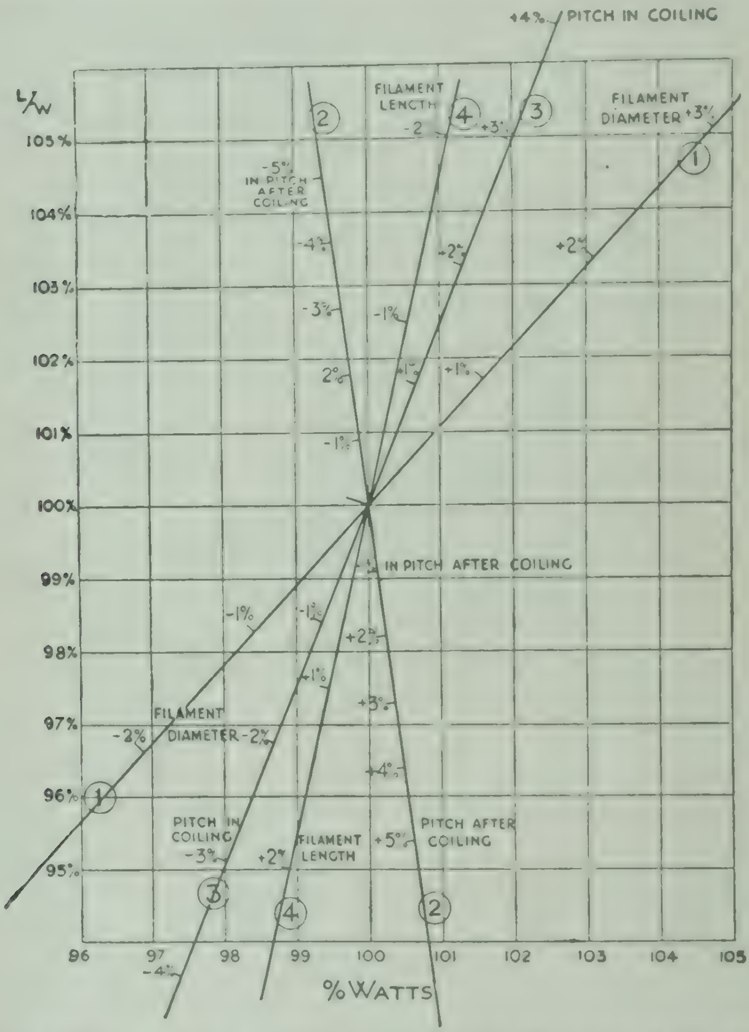


FIG. 17.—Effect of Errors in Filament Dimensions on Watts and Lamp Efficiency.

nitro-cellulose binder, and the completed electrode is placed inside a coated glass tube and sealed in. The tubes are then exhausted, "dosed" with mercury, and filled with argon. During the exhausting process the tubes and electrodes are subjected to a temperature of 480° C., which removes from the glass and components all occluded gases. Before sealing, a small amount of argon is introduced into the lamps.

The efficiency of the hot cathode tube is greatly in excess of that of the earlier cold cathode tubes and a greater intensity of light is obtained. This makes possible their use for beacon lights for aerodromes, particularly since the orange red colour, obtained with neon as the ionising gas, has the power of penetrating mist and light fogs. Neon and argon are used as filling gases for sodium or mercury vapour discharge tubes, the light obtained from the ionised gas being coloured by the metals after their vapour pressure has been increased sufficiently by heat.

SECTION LXXXIII

URANIUM

By Norbert Berkowitz

LITERATURE

P. Pascal.—"Traité de Chimie Minérale," Vol. XI, 1932.

H. A. Doerner.—"Notes on the Extraction of Radium, Vanadium, and Uranium from Carnotite." U.S. Bur. Mines, Rep. Invest. 2873.

G. H. Dieke and A. B. F. Duncan.—"Septroscopic Properties of Uranium Compounds." McGraw-Hill Book Co., Inc., New York, 1949.

J. A. De Ment and H. C. Dake.—"Uranium and Atomic Power." Chem. Publ. Co. Inc., New York, 1945.

H.M.S.O.—"Handbook of Chemical Methods for Detection of Uranium in Minerals and Oils." London, 1950.

W. F. James, A. H. Lang, R. Murphy, and S. N. Kesten.—"Canadian Deposits of Uranium and Thorium." *Min. Eng.*, **187**, 239 (1950).

A. Jaeschke.—"Red Glazes with Uranium." *Keram. Z.*, **1**, 57 (1949).

F.I.A.T. 795.—Compounds of Lanthanum, Neodymium, Praseodymium and Uranium in Germany.

Uranium (U; atomic weight 238.07; atomic number 92) is the heaviest of the naturally occurring elements, and related to radium, actinium and thorium in many of its physical properties. Uranium oxide was first isolated by Klaproth in 1789 from Pitchblende, and the metal by Péligot in 1842.

In the earth's crust, uranium occurs only to the extent of about four parts per million, but uranium ores are very widely distributed, and up to date more than sixty crystalline and amorphous uranium-bearing minerals have been reported. The most important of these, and the ones from which uranium has so far been mainly extracted, are Pitchblende (also known as Uraninite) and Carnotite.

Pitchblende, which may contain as much as 80 per cent. of uranous-uranic oxide (U_3O_8), occurs mainly in metalliferous veins, either in a crystalline or in an amorphous massive form. The crystalline form (Octahedral, or occasionally cubic) is relatively rare, has a hardness of 5.5 and a specific gravity lying between 9.0 and 9.7. The amorphous, massive form has a lower specific gravity, from 6.4 upwards, and almost certainly represents an altered form. The lustre of Pitchblende ranges from sub-metallic to dull pitch black and its colour from greyish to velvet black. Apart from the uranous-uranic oxide, it also contains appreciable proportions of lead. The crystalline form further contains some thorium (or zirconium) and frequently metals of the lanthanum and yttrium groups; these, however, are absent in the massive form. In addition, both forms of Pitchblende contain small quantities of radium and helium (representing breakdown products of uranium) and up to 2.6 per cent. of nitrogen and argon.

Carnotite is a hydrated potassium uranyl vanadate containing between 2 per cent. and 4 per cent. of U_3O_8; its empirical composition has been given as $K_2O.2U_2O_3.V_2O_5.2H_2O$. It generally occurs as yellowish incrustations in sandstones and other quartzose materials.

In addition to these two minerals, uranium also occurs frequently in combination with certain rare earths: thus eight tantalo-niobates of uranium have been reported, as well as several titanates of yttrium and uranium, silicates of uranium and thorium, uranates of vanadium and calcium, and three or four uranyl phosphates; an example of the last-named group is Autunite, to which the empirical formula $Ca(UO_2)_2(PO_4)_2 8H_2O$ has been assigned.

Geographical Distribution of Uranium Ores.—Pitchblende is generally a primary constituent of granitic pegmatites. In Europe, important deposits occur in Roumania (Rézbánya; in Czechoslovakia (Joachimsthal and Pribram); in Germany (at several localities in Saxony), and in Norway (near Moss and Raade). Minor deposits occur in Britain (Cornwall and, according to a very recent claim (August 1950), at Dolgelly in Wales). In the United States, deposits of Pitchblende have been reported in Connecticut, North Carolina, Texas, and Colorado; in Canada an important deposit is worked in the Great Bear Lake district; and more recently extensive deposits are being exploited in Africa (Belgian Congo, Rhodesia, and Tanganyika Territory).

Workable deposits of Carnotite have been reported from Pennsylvania, from the South-Western districts of Colorado, and the neighbouring districts of Utah (in the United States); from the Belgian Congo (near Katanga).

Other occurrences of uranium ore are known in British Guiana, New Zealand, and Portugal. New discoveries are also reported from Russia and the Northern Territory of Australia (near Fergusson River), and in Sweden uranium is a by-product of the shale oil industry. Uranium is also now being recovered from the waste dumps of the gold mining industry, particularly in the Rand districts of South Africa.

Complete production figures for uranium are not available, in view of security restrictions imposed upon most countries. It may, however, be of interest to note that the 1939 production of metallic uranium by the United States Vanadium Corporation amounted to 59,300 lbs., and that resumption of mining by the Union Minières in the Belgian Congo in 1942 resulted in an output of over 1,000 metric tons of ore containing (according to the U.S. Bureau of Mines) 695.6 metric tons of U_3O_8.

Table I summarises the composition, occurrence, and properties of radioactive ores containing uranium and other metals. Thorium ores, containing smaller proportions of uranium, are given in a related table in the section on Thorium. These tables are based upon the "Abridged Table of Uranium and Thorium Minerals," by Nucleonic and Radiological Developments Ltd.

Manufacture of Metallic Uranium

(*a*) **Treatment of Ores.**—In order to render crude uranium ores suitable for the extraction of the metal, it is generally necessary to roast the ore to remove sulphur, arsenic, and molybdenum, and then to heat it in a reverberatory furnace with sodium carbonate and a little sodium nitrate. The fused mass thus obtained is then cooled, washed with water, extracted with dilute sulphuric acid and filtered. The filtrate,[1] which contains all the uranium, is then treated with sodium carbonate in order to precipitate the basic carbonates of iron, aluminium, nickel, and cobalt. These precipitates are again filtered off and the uranium in the filtrate precipitated either by the addition of sodium hydroxide or by adding dilute sulphuric acid and vigorously boiling the solution. In both cases the resultant product is sodium diuranate; the commercial salt has the composition, $Na_2U_2O_7$, $6H_2O$.

If it is desired to produce the black uranous-uranic oxide U_3O_8, the sulphuric acid extract obtained from the fused mass, after heating in the reverberatory furnace, is first treated with hydrogen sulphide in order to remove arsenic, antimony, copper, lead, and bismuth; filtered; the filtrate oxidised with nitric acid, and finally rendered alkaline by the addition of an excess of ammonia. The precipitate, which consists of ferric hydroxide and ammonium uranate, is then digested with a concentrated solution of ammonium carbonate, containing an excess of ammonia, in order to dissolve ammonium uranate. Ferric hydroxide is removed by filtration of the hot solution and, on cooling, the filtrate of ammonium uranyl carbonate crystallises out. A further quantity of ammonium uranate can be obtained from the mother liquor by adding ammonium sulphide in order to precipitate zinc, nickel, and cobalt as the sulphides, filtering the mixture, and evaporating the filtrate to dryness. Both products yield U_3O_8 on ignition.

---

[1] The insoluble residue obtained by filtration is used for the extraction of radium.

(*b*) **Reduction of Ores.**—Prior to the second world war, metallic uranium was commonly prepared by reducing the oxide, U_3O_8, with sugar charcoal in an electrically heated carbon tube; the proportion of oxide to charcoal being roughly 12 : 1. The product thus obtained, however, usually still contained an appreciable percentage of carbon.

More recently, therefore, particularly since large quantities of metallic uranium are used in fission work in connection with the production of nuclear energy, the metal has been obtained in powder form, of about 98 per cent. purity, by heating an intimate mixture of the oxide with calcium hydride to 980° C. Lime produced in this reaction is removed by means of dilute acid and the residual metallic powder thoroughly leached with water and dried *in vacuo*. To convert it into a more solid form, it is then briquetted and sintered in hydrogen at about 1,000° C. or, alternatively, melted *in vacuo*.

A second modern process, which appears to gain increasing importance, consists in reducing the tetrachloride, UCl_4, with sodium, potassium or calcium in an externally heated container.

A third process consists in electrolysing potassium uranium fluoride in a bath of fused calcium and sodium chlorides. The spongy metal deposited on the cathode is then treated in the same way as the metal powder obtained from the reduction of the oxide with calcium hydride.

Uranium metal prepared by these methods has a silvery white, lustrous appearance and a specific gravity of 18.7. It melts, according to recent determinations, at 1,689° C., but is in this region considerably more volatile than iron. When heated in air it remains unattacked up to about 170° C., at which temperature it begins to burn brilliantly. It does, however, readily react with boiling water, yielding the hydroxide, and with most mineral and even with several organic acids. Salts of uranium are characterised by their very strong fluorescence.

Utilisation of Uranium.—During recent years all previous applications of uranium and its compounds have been dwarfed by its use in the production of atomic energy. This aspect is dealt with more fully in Sections LXXXV and XC. Here it need only be pointed out that metallic uranium consists of a mixture of isotopes (see Section LXXXV), one being the U.238 isotope and amounting to about 99.3 per cent., and the second the U.235 isotope, which amounts to 0.7 per cent. For the production of atomic energy only the U.235 isotope is employed, and this is separated, as explained more fully in Section LXXXV, by gaseous diffusion or thermal diffusion.

One or two minor uses of uranium may, however, be mentioned. Because of its strong fluorescence, the oxide has been used for the preparation of yellow glasses possessing a green reflex, as well as for the production of glasses possessing low coefficients of thermal expansion (*e.g.*, for glass to metal contacts in radio tubes). In the former case about 20 per cent. of the oxide is normally required.

Several uranium salts are also used as mordants, particularly for silk; their suggested use as wool mordants appears to be connected with several practical difficulties and little progress seems to have been made in this direction.

The metal itself has proved particularly suitable in certain glow discharge lamps and has also been used in the production of special steels in which it acts as a carbide stabiliser; as a result, the carbides remain uniformly distributed throughout the matrix so that the resultant hardness is not accompanied by brittleness. It is, however, doubtful whether uranium steels have any real advantage over the modern **tungsten** and **titanium** steels which are rather cheaper to produce.

TABLE I.—OCCURRENCE OF RADIOACTIVE ORES

Name and Composition.	Occurrence.	Known Deposits.	Structure.	Colour, Lustre.	S.G.	H.	%.	Remarks.
AUTUNITE (S.). Hydrated phosphate of calcium and uranium.	Pegmatite dykes with torbernite and uraninite also as gossans to lode deposits.	Devon, Cornwall, France, Czechoslovakia, U.S.A., Portugal, Australia.	Orthorhombic tabular, or flaky crystals.	Lemon yellow, pearly.	3.1	2 to 2.5	55 to 62	Associated with URANINITE to which it may be a pointer.
BECQUERELITE. Hydrous uranium oxide.	In siliceous outcrops amongst magnesian limestones.	Kasolo in Belgian Congo.	Orthorhombic small crystals.	Brown, yellow, resinous.			86.5	Associated with other uranium bearing minerals, also copper.
BLOOMSTRANDINE (P). Niobates and titanates of uranium plus rare earths.		Norway, Sweden, South Africa.	Orthorhombic tubular crystals.	Brownish black.	4.8			Also known as PRIORITE.
BLOOMSTRANDITE (P). A hydrous titanotantalo-niobate of calcium iron and uranium.	Pegmatites.	Sweden, Urals, Madagascar.	Octahedral or massive.	Black.	4.2	5.5	20	Believed to be related to BETAFITE.
BRANNERITE. Uranium and titanium oxides.	Amongst alluvial gravels containing gold.	Stanley Basin, Idaho, U.S.A.	Water worn pebbles.					
BROGGERITE (P).		Annerod, Norway.	Isometric octahedral crystals.				75	Variety of uraninite (contains thorium).
CARNOTITE (S). Hydrated vanadate of uranium and potassium.	In shale, gneisses, and sandstones, also flat lying carbonaceous sandy beds, replacing fossil wood and bitumen in the sandstone.	U.S.A. and South Australia.	Orthorhombic very fine crystals, sometimes flaky.	Canary or bright lemon yellow.			1.64	of uranium oxides. May be a pointer to primary U. Occurs as a powder filling rock cavities, or as botryoidal crusts.
CLARKEITE (S). Sodium lead uranium oxide.		U.S.A., North Carolina.	Massive.	Dark brown, waxy.	6.4	4 to 4.5	80	Derived from uraninite by hydrothermal alteration. Conchoidal fracture.
CLEVEITE (P).		Norway.					60	Variety of uraninite, but with 10 per cent. rare earths and much helium.
CURITE. A hydrous lead oxide.	Dolomite or magnesian limestone.	Belgian Congo.	Orthorhombic minute needle-like crystals.	Reddish brown.	7.19	4 to 5	73	Discovered owing to presence of TORBERNITE in the copper veins.
ELLSWORTHITE. Hydrated calcium, [illegible]		Canada.	Isometric.	Dark yellow to dark brown.	3.6 to 3.7	4	22	
EUXENITE (P). Niobate and titanate of yttrium, cerium, erbium and uran-	Pegmatites and "placer" gold and tin localities.	Norway, Finland, Sweden, Brazil, Green-	Massive or orthorhombic.	Black, green or brown.	5	6.5	14	Fracture conchoidal.

				vitreous.				
GUMMITE (S). Oxides of uranium with lead and thorium.	See Uraninite.	Joachimsthal (Czechoslovakia), Belgian Congo, U.S.A., Sweden.	Amorphous or botryoidal (resembles gum).	Yellow, orange, reddish brown or black, waxy or greasy.	3.9 to 4.2	2.5 to 3.0	75	Indicator of uraninite, of which it is an oxidation product. Fracture conchoidal to uneven.
HATCHETTOLITE. Hydrous titano-tantalite of uranium, calcium, iron, etc.	Pegmatites.	U.S.A., India, Madagascar.	Isometric or octahedral.	Yellow brown to dark brown, resinous.	4.7 to 4.9	5	15	
KOLM (P).	Carbonaceous deposits in upper Cambrian oil shales or alum shales.	Sweden.	Resembles coal or jet.	Black.			0.5	Uranium metal obtained from ash after burning.
PITCHBLENDE (P). Uranium oxides with impurities.	Associated with metalliferous veins of copper, silver, cobalt, nickel, bismuth, vanadium, lead, tin, etc., usually sulphides and arsenides.	Saxony, Cornwall, Canada, Congo, Joachimsthal, U.S.A., U.S.S.R., etc.	Amorphous or botryoidal.	Black opaque, pitch-like, greasy or dull.	6.5 to 8.5	5 to 6	90	Frequently covered with bright yellow, orange, red and green halo. See URANINITE, of which it is the colloform variety. Biggest finds have been associated with hydrothermal injections in dolomitic limestones (Belgian Congo) or igneous intrusions very altered pre-Cambrian sediments and volcanics (Great Bear Lake).
POLYCRASE (P). Niobate and titanate of rare earths and uranium.		Norway, Sweden, Brazil, U.S.A.	Orthorhombic.		4.9 to 5.0	5 to 6	20	Very similar to EUXENITE.
SAMARSKITE (P). Tantalo-niobate of yttrium, cerium, calcium, iron, uranium and other constituents.	Granite, pegmatites.	Russia, Norway, Madagascar, India, Brazil, U. S. A., Western Australia.	Orthorhombic, sometimes prismatic crystals, more often massive.	Black, sub-vitreous.	5.6 to 5.8	5.5	17	Somewhat similar to FERGUSONITE.
TANTALO-POLYCRASE (P).		Western Australia.	Often in angular fragments.	Brownish black to dark bronze, resinous.	5.4 to 5.9		7	Conchoidal fracture.
TORBERNITE (S). Hydrated phosphate of uranium and copper, often with arsenic replacing part of the phosphorus.	Generally in outcrops of uranium deposits, especially those in pegmatites, and as sulphide lodes.	Joachimsthal, Saxony, England, S. Australia, Belgian Congo, Great Bear Lake.	Orthorhombic crystals generally in thin tubular mica-like plates.	Bright green (emerald to grass green), pearly.	3.2 to 3.7	2 to 2.5	60	Probably most abundant secondary mineral. Metatorbernite variety containing less water. Sometimes known as CHALCOLITE and copper uranite. Translucent to transparent.
URANINITE (P and S). Crystalline uranium oxides, UO_2, U_3O_8 and UO_3, plus variable amounts of thorium and lead, rare earths, helium, argon, etc.	Pegmatites as a primary and as a secondary amongst sulphide of silver, lead, iron, zinc, and copper, etc. Very widely distributed.	Joachimsthal, Belgian Congo, Canada, etc.	Isometric, usually found in cubical or octahedral crystals very occasionally of large size.	Greyish, greenish brownish or velvety black, sub-vitreous.	8 to 10	5 to 6	90	U_3O_8. Very similar to pitchblende though generally heavier. Pitchblende is the non-crystalline form of uraninite. Both are soluble in nitric and sulphuric acid.
ZIPPEITE (S). Hydrated uranium sulphate.		Joachimsthal, Canada, U.S.A.		Bright yellow.				Associated with CARNOTITE and with asphaltic sandstones, or with exposed PITCHBLENDE, of which it is an alteration product.

P = Primary. S = Secondary. S.G. = Specific gravity. H. = Hardness (Moh's scale.) % = Percentage of uranium or thorium oxides.

SECTION LXXXIV

VANADIUM

By Norbert Berkowitz

LITERATURE

J. A. N. Friend.—"Textbook of Inorganic Chemistry," Vol. VI, Pt. 3, 1929.
P. Pascal.—"Traité de Chimie Minérale," Vol. IV, 1933.
H. A. Doerner.—"Notes on the Extraction of Radium, Vanadium, and Uranium from Carnotite." U.S. Bur. Mines, Rep. Invest. 2873.
Science Museum, London.—Vanadium: Occurrence, Mining, Extraction and Metallurgy. Science Libr. bibliogr. series No. 389.
P. Dickens and G. Thanheiser.—"Bestimmumng von Eisen und Vanaden, etc." Kaiser Wilhelm Inst. f. Eisenforschung, Dusseldorf, Vol. XIV, 1932.
M. M. Parks.—"Gravimetric Method for the Quantitative Estimation of Vanadium." Diss., Columbia College, New York, 1930.
D. Bertrand.—"The Biogeochemistry of Vanadium." Amer. Mus. Nat. Hist. Bull., Vol. XCIV, 1950.

Vanadium (V; atomic wright = 50.95; atomic number = 23) is not an abundant element, but relatively widely disseminated. Of the thirty-five vanadium minerals so far reported, the most important are Patronite, Carnotite, Roscoelite, and Vanadinite. Patronite is a complex ore consisting mainly of a greenish sulphide of vanadium with an approximate composition VS_4. It is amorphous and almost invariably black, due to the presence of large quantities of carbonaceous matter. The specific gravity of Patronite is about 2.71 and its hardness 2.7. It is frequently found associated with pyrites and free sulphur, and on calcination will burn readily and may lose up to 45 per cent. of its initial weight. The main source of Patronite derives from Peru (near Cerro de Pasco).

Carnotite is a hydrated potassium uranyl vanadate already described under Uranium (see Section LXXXIII). This mineral is found in large quantities at various localities in Colorado and the neighbouring districts of Utah, where it is mined for its vanadium and uranium contents, as well as for the small proportion of radium present in it. Other deposits of carnotite occur in the Belgian Congo and near Olary in South Australia.

Roscoelite is a vanadium-bearing muscovite mica in which part of the aluminium has been replaced by vanadium. The hardness of Roscoelite is 2.5, its specific gravity 2.97, and its colour clove brown to greenish-brown. It occurs mainly in California (particularly at the gold mines in Eldorado County) and probably forms the most important vanadium ore produced in the United States. It has, however, been reported from Western Australia (Kalgoorlie).

Vanadinite is a chloro-vanadate of lead whose composition has been reported as lying between the limits $Pb_4.PbCl(VO_4)_3$ and $9PbO.3V_2O_5.PbCl_2$. Its composition would thus correspond to a vanadium oxide content of up to 19.4 per cent. The hardness of vanadinite varies between 2.75 and 3.0, its specific gravity between 6.66 and 7.10, and its colour from reddish-brown to straw yellow; a deep ruby red variety has also been reported. The mineral is sub-translucent to opaque. In general, vanadinite occurrences are confined to altered lead deposits. Important deposits are found in the Ural Mountains of Russia, in the Corinthia district of Austria, and in the province of Andalusia in Spain. In the United States the mineral is frequently found in the mining regions of Arizona and New Mexico.

Of the other vanadium minerals only Descloizite is of importance as a source of vanadium. This mineral is a hydrated mixture of vanadium pentoxide and oxides of lead and zinc, the latter usually in the ratio of 1 : 1. Descloizite is a mineral of secondary origin, occasionally found associated with lead-zinc deposits. Small accumulations of the mineral have been reported from Austria, from Rhodesia, and from South West Africa, but it appears that the mineral is only worked in the River Plate district of Argentina.

Extraction of Vanadium from its Ores

Owing to the range and complexity of vanadium-bearing minerals and the somewhat erratic behaviour of these ores during extraction, the extraction methods vary widely. It may therefore be helpful to indicate briefly some of the major processes that have been used in the past, and one or two at present in use, in the more important vanadium producing centres.

Broadly speaking, extraction processes may be classified into (1) acid extraction processes, and (2) alkali extraction processes. The general concensus of opinion now favours the latter since the resultant alkaline vanadates are stated to be less erratic in their behaviour than the vanadyl compounds obtained from acid extractions. In addition to these two groups, moreover, a number of methods have been described which aim at the recovery of vanadium from the extraction (or "mill") solutions.

(1) **Acid Extraction Processes.**—A method claimed to be suitable for Roscoelite, vanadiferous sandstone, and similar minerals has been protected in the United States by Koenig in Patent No. 986,180. According to this, the crushed ore is treated with a 20 per cent. solution of a mineral acid, such as sulphuric or hydrochloric acid, at about 200° C. and a pressure of 225 lbs. per square inch. After some hours the solution thus obtained is filtered and evaporated to near dryness. The resultant solid residue of salts is then heated to bright redness in order to expel residual acid, the solid residue of oxides (and sulphates if sulphuric acid is used in the first extraction) mixed with sodium carbonate and roasted at red heat in an oxidising atmosphere with or without the addition of oxidising agents. The roasted mass is treated with boiling water and carbon dioxide in order to precipitate aluminium.

In the Fleck method (U.S. Patent 880,645) the finely crushed ore (which is usually Carnotite, but may consist of other vanadium-bearing ores) is treated with dilute sulphuric acid in order to dissolve uranium, vanadium, copper, and iron, the clear solution decanted and treated with sulphur dioxide in order to reduce iron and vanadium compounds to the ferrous and vanadous states. A calculated quantity of powdered limestone is then added until the metals begin to separate, the solution freed from precipitated calcium sulphate by filtration, and precipitation of the metals completed by boiling the solution with a further quantity of limestone. The resultant precipitate is stated to contain about 20 per cent. of uranium and vanadium oxides.

In a third process (U.S. Patents 1,020,224 and 1,020,312, 1912; English Patent 6,119, 1912) the ore is also extracted with dilute sulphuric acid, but the solution nearly neutralised and then treated with an oxidising agent, such as ammonium persulphate, chlorine or an oxy-acid of chlorine, in order to precipitate vanadium.

(2) **Alkaline Extraction Processes.**—In general these methods aim at the production of soluble sodium vanadate, either by treating the ore with aqueous solutions of sodium carbonate or hydroxide, or by roasting it with sodium chloride. The efficiency of extraction in some of these methods is as high as 92 per cent. Some typical processes are as follows:—

(*a*) The crushed ore is mixed with crude sodium chloride and dried until its moisture content is about 1 per cent. The caked mass is then reground, roasted, lixiviated with water, and vanadium precipitated from it as ferrous vanadate by the addition of an excess of ferrous sulphate.

(*b*) Vanadite ore is fused with an alkali carbonate, sulphate, or sulphide in a reverberatory furnace in order to produce argentiferous lead and a slag carrying the vanadate aluminate and silicate of sodium as well as ferric oxide. This slag is separated, the sodium vanadate in it fully oxidised by blowing air through it, and the oxidised mass granulated by pouring into boiling water. The solution obtained by extracting the granular product with further quantities of water contains all the sodium vanadate, some sodium silicate but no aluminate. Silicate is then removed by evaporating a portion of the liquid to syrupy consistency, adding sulphuric acid to it in order to precipitate part of the vanadic acid and then adding the whole of this treated fraction to the untreated portion of the vanadate-bearing mother liquor. The solution is then passed through a filter press in order to remove precipitated silica, the filtrate evaporated to expel excess sulphuric acid, and the residue carefully washed with water. The product consists of relatively pure vanadic acid, and it is stated that the yields to be obtained by this process vary between 92 per cent. and 95 per cent. of the vanadium content of the starting material.

(*c*) According to a French process developed by A. H. Perret (British Patents 26,777, 1910, and 15,181, 1911), the ore is roasted with an alkali carbonate and oxidising conditions maintained after adding sodium nitrate to the mixture. The fused mass is then granulated by running into cold water and thoroughly stirred. The solution, which contains all the vanadium, may then be treated with ammonium chloride to yield ammonium meta-vanadate, or vanadic acid may be precipitated by the addition of mineral acid.

Methods described for recovering vanadium in the extraction, or "mill", solutions consist in precipitation (1) as ferrous vanadate by nearly neutralising the solution and adding ferrous sulphate; or (2) as calcium vanadate by adding slaked lime; or (3) recovering the metal by electro-deposition. According to several investigators, the third method, *i.e.*, electro-deposition, has several advantages over the other two, even though part of the impurities present in the original solution will nearly always be found in the final product.

Among currently used methods for the extraction of vanadium from vanadium ores, two in particular may be mentioned here. In the first, which is used in the United States by the Anaconda Copper Mining Co., vanadium is produced from phosphate rock, which contains as little as 0.3 per cent. of the pentoxide V_2O_5. The principle of the method consists in precipitating vanadium as phospho-vanadic acid, treating this with milk of lime and sodium carbonate to obtain sodium vanadate, and finally reacting this product with sulphuric acid. The end product is a so-called "red cake," which contains over 90 per cent. of vanadium pentoxide; it is stated that this process gives a recovery of 65 per cent. of the metal contained in the starting ore, but that the high loss is justified by the simplicity of the process.

The second process, which employs Peruvian Patronite, is based on the fact that by far the largest proportion of metallic vanadium currently produced is employed in the manufacture of vanadium steels. According to this process, the ore, which consists of a mixture of vanadium sulphide, free sulphur, and hydrocarbons, is roasted to produce a clinker containing about 40 per cent. of vanadium oxide practically free from sulphur. This oxide is then reduced by carbon in an electric furnace and the product treated with molten steel; in this way ferro-vanadium master alloys containing up to 50 per cent. of vanadium can be obtained.

Properties of Metallic Vanadium.—Pure metallic vanadium is a white, extremely hard metal which has a specific gravity of 5.68 and a melting point of 1,720° C. (3,128° F.). Its specific heat over the range 0–100° C. is 0.1153. It is unaffected by air or water at ordinary temperatures but on heating combines rapidly with both oxygen and nitrogen, forming a series of oxides and nitrides. Its affinity for oxygen is also shown by the fact that whilst it is almost wholly unaffected by hydrochloric, hydrofluoric, and sulphuric acids, it will dissolve violently in oxidising acids, such as nitric, chloric, or perchloric acids.

Vanadium and its Compounds in Industry. Of the world's total output per annum, some 3.000 metric tons, produced mainly in Peru (32 per cent.), the United States (27 per cent.), South West Africa (21 per cent.), and Northern Rhodesia (14 per cent.), well over 90 per cent. are finding application in the production of vanadium steels. Metallic vanadium is, like titanium, a powerful cleansing agent and will also increase very greatly the hardness of quenched carbon steels, and steels of low alloy content; an example of the latter are the chromium steels containing between .5 per cent. and .7 per cent. of chromium. It is also reported that whilst vanadium does not increase the hardness after water quenching alloy steels with a higher alloy content, such steels are greatly improved by an addition of vanadium when they are cooled at a slower rate or tempered within a certain (and usually specific) temperature range.

Furthermore, when vanadium steels are cooled rapidly and re-heated to between 500°–700° C. pronounced temper hardening occurs. The full effect of this temper hardening can be obtained with as little as .35 per cent. to .40 per cent. vanadium, but the extent of temper hardening will depend upon the composition of the steel and its previous history.

In cast iron, vanadium acts also as a strong carbide stabiliser and hence tends to increase hardness and depth of surface chill. For example, a cast iron containing 3.15 per cent. of carbon and 1.8 per cent. of silicon can be chilled to give a hardness of 490 Brinell at the surface and a hardness of about 300 Brinell at a distance of $\frac{3}{8}$ in. below the surface; by the addition of 0.1 per cent. of vanadium the surface hardness is increased to 510 and even at $\frac{3}{4}$ in. below the surface it remains as high as 480. With a suitable composition of the basis metal a very marked increase in tensile strength, up to 25 per cent., can also be obtained by an addition of vanadium.

As also indicated above, the addition of vanadium to steels is generally achieved via a ferro-vanadium master alloy. These are usually made to contain 40–50 per cent. of vanadium and have a melting point between 1,480° C. and 1,500° C. Master alloys containing smaller proportions of vanadium melt at correspondingly lower temperatures up to 30 per cent. vanadium (1,425° C.). A still further reduction in the vanadium content results in gradually increasing melting points; a ferro-vanadium alloy containing 25 per cent. vanadium thus melts at 1,450° C.

Because of their extreme hardness and their ability to maintain their temper on heating, vanadium steels, generally incorporating a small proportion of chromium, find use for the manufacture of high speed tools and other hard wearing shock-resisting metal surfaces.

To a lesser extent, vanadium metal is also used in the production of **non-ferrous alloys.** For example, the addition of a small quantity of vanadium to Al—Cu—Mg—Ni alloys has been claimed to refine the grain structure and improve the casting properties, whilst at the same time raising impact strength and improving response of the alloy to heat treatment.

Vanadium **compounds** have not yet found very extensive use, though several applications have been suggested.

Vanadium pentoxide, V_2O_5, usually supported on alumina, pumice, or ferric oxide, is thus used as a **catalyst** to promote the oxidation of sulphur dioxide to trioxide in the manufacture of sulphuric acid, and also the oxidation of ammonia in the manufacture of nitric acid.

To a limited extent vanadium salts have also been used for colouring **pottery** and **glass** and as mordants in calico printing, and for fixing aniline black on silk.

The use of ammonium vanadate in **leather dyeing** has also been described.

In **photography,** vanadium salts, particularly vanadium chloride, have been used for toning silver bromide prints to a green colour. According to United States Patent 979,887, 1910, this is achieved by mixing 500 gm. of liquid vanadium chloride with 1,300 gm. of anhydrous oxalic acid, compressing the product into tablets, and preparing toning baths by dissolving 3.8 gm. of this product, together with 1.5 gm. of anhydrous oxalic acid, 1 gm. of ferric oxalate, and 1 gm. potassium ferri-cyanide in 1 litre of water.

The suggestion that solutions of vanadium salts can also be used for the manufacture of **writing inks** has not so far been exploited. It has been shown that whilst the colour of such inks is unaffected by acids, alkalis or chlorine, it is not a permanent colour.

Analysis of Vanadium Ores and Alloys

A volumetric and a colorimetric method are available for analysis, but the latter can only be applied to tungsten-free samples containing less than 3 per cent. of chromium. The two methods are briefly described below.

(1) **Volumetric Method.**—Transfer the weighed sample (see note 1) to a 300 c.c. flask, add 40 c.c. of dilute sulphuric acid (1 : 4), and digest until vigorous reaction ceases. Then add 1–4 c.c. of HF to complete the decomposition, oxidise the resultant solution by slow addition of nitric acid (sp. gr. 1.42), heat to boiling and dilute to 100 c.c. with water. Add 1 gm. of ammonium persulphate, boil for five minutes, and cool slightly. Now add N/10 ferrous ammonium sulphate from a burette until all chromium and vanadium present are fully reduced. Cool, oxidise the vanadium with potassium permanganate until a permanent pink colour is observed, and finally destroy the excess permanganate by the addition of a 5 per cent. solution of sodium nitrite; care must be taken in this operation to use only a very slight excess of nitrite. Add 2 gm. of urea and allow to stand for five minutes. Finally, add 5 c.c. of hydrofluoric acid and a few drops of diphenylamine sodium sulphonate indicator. Allow the purple colour to develop and titrate with N/51 ferrous ammonium sulphate until the addition of 1 drop changes the colour to green. The vanadium content is then given by the expression

$$\text{Percentage V} = \frac{\text{A} \times 0.1}{\text{Wt. of sample}}$$

where A is the number of c.c. of N/51 ferrous ammonium sulphate.

Note.—

1. If the vanadium content is less than 1 per cent., use 2 gm. of sample. If between 1 per cent. and 2 per cent., use 1 gm. of sample, if greater than 2 per cent., use 0.5 gm. of sample.

(2) **Colorimetric Method.**—Transfer 1 gm. of the sample to a 400 c.c. tall beaker and dissolve in 15 c.c. of dilute 1 : 4 sulphuric acid. When the reaction is complete oxidise with 10 c.c. of nitric acid (sp. gr. 1.42) and boil to expel nitrous fumes. Dilute to 150 c.c. with distilled water and heat to boiling. Then add potassium permanganate solution (1.2 per cent.) until a permanent pink colour is observed or a brown precipitate is formed, and boil for five minutes. Add a slight excess of saturated sulphurous acid, boil to expel sulphur dioxide, cool, add 10 c.c. of dilute 1 : 1 phosphoric acid and 5 c.c. of hydrogen peroxide (10 vols.).

Prepare a blank solution for comparison by treating a vanadium-free steel in the same manner. (If the sample under test contains nickel, chromium, cobalt, or molybdenum, add an equivalent quantity of these metals to the blank before testing; see note 1). Transfer the solutions to graduated comparison cylinders (see note 2) and add standard ammonium meta-vanadate solution to the blank;

the additions should be made in small quantities from a burette and the solution should be left for at least two minutes after each addition in order to permit the colour to develop fully. Continue the additions until the colour of the blank intensities and sample solutions are identical at equal dilution. The percentage of vanadium in the sample is then given by the expression

$$\text{Percentage V} = \frac{\text{A} \times 0.05}{\text{Wt. of sample taken}}$$

where A is the number of c.c. of the standard vanadate solution.

To prepare the ammonium meta-vanadate solution, dissolve 1.148 gm. of reagent in hot water, cool, and dilute to 1 litre. One c.c. of this solution then contains 0.0005 gm. of vanadium.

Notes.—

1. Add nickel, chromium, and cobalt as solutions of their sulphates. If the molybdenum content exceeds 0.5 per cent., its equivalent is added as ammonium molybdate.
2. If titanium present, add 3 c.c. of HF to both sample and standard solutions in order to destroy the colour produced by hydrogen peroxide.

SECTION LXXXV

RADIOACTIVE SUBSTANCES

By Norbert Berkowitz

LITERATURE

M. Curie.—"Radioactivité." Paris, 1935.
L. Gmelin.—"Handbuch der Anorganischen Chemie," 8th ed., system No. 31.
Sir J. Chadwick.—"Radioactivity and Radioactive Substances." London, 1921.
G. von Hevesy and F. A. Paneth.—"Manual of Radioactivity." Oxford Univ. Press, 1938.
G. Friedlander and J. W. Kennedy.—"Introduction to Radiochemistry." Chapman & Hall, London, 1949.
Science Museum, London.—Radioactivity; Short List of Textbooks. Science Libr. Bibliogr. Ser. No. 45, 1932.
A. D. Little, Inc.—"Selected Bibliography on Industrial Uses of Radioactive Materials." Cambridge, Mass., 1949.
E. Broda.—"Advances in Radiochemistry and in Methods of Producing Radio-Elements by Neutron Irradiation." Cambridge Univ. Press, 1950.
F. W. Aston.—"Mass Spectra and Isotopes."
United States Atomic Energy Commission.—Bibliography on Isotope Utilisation, 1948.
A. Strohl and M. Berger.—"Les Isotopes Radioactifs en Biologie." Paris, 1946.
G. von Hevesy.—"Radioactive Indicators." Interscience Publishers, London, 1948.
C. Voegtlin and H. C. Hodge.—"Pharmacology and Toxicology of Uranium Compounds." McGraw-Hill Book Co. Inc., New York, 1949.

INTRODUCTION

In the course of research into the nature of X-rays, H. Becquerel (1895) observed that uranium salts were capable of fogging photographic plates in the dark, and —like X-rays—of ionising air. He accordingly concluded that these salts emitted a hitherto unknown form of radiation and suggested the term "radioactivity" for this phenomenon. Shortly afterwards similar observations were reported with metallic uranium and pitchblende, a uranium ore consisting mainly of U_3O_8 (P. and M. Curie, 1898), with thorium salts and metallic thorium (G. C. Schmidt, 1898; M. Curie, 1898), and with three new elements eventually isolated from pitchblende after separation of the uranium: Polonium (P. and M. Curie, 1898), Radium (P. and M. Curie and G. Bemont, 1898), and Actinium (A. Debierne, 1898; F. Giesel, 1901). In each case it was shown that the intensity of the radioactive emission was characteristic of the element, and that it was independent of experimental conditions and the previous history of the sample. Radioactivity was consequently regarded as an *atomic* phenomenon.

These observations, which have only recently begun to gain industrial importance, have profoundly influenced the development of atomic physics. The most important consequence, the possibility of using nuclear fission as a source of energy, is considered more fully in Section XC. Here we shall confine ourselves to some general aspects of the physics and chemistry of radioactive substance.

The Nature of Radioactive Emissions.—Until Becquerel's discoveries, it was generally assumed that atoms were indestructible, and that the atoms of different elements were radically different. Becquerel's, and later more systematic work, has rendered these beliefs wholly untenable and shown (*a*) that all atoms are built up of the same fundamental particles and (*b*) that the atom resembles a miniature planetary system.

From the behaviour of the radiations emitted from radioactive substances in a magnetic field it can be demonstrated that the radiations fall into three classes.

The first of these, known as alpha-radiation (Rutherford, 1899), possesses relatively low penetrating power, can be appreciably deflected in a magnetic field, and is strongly ionising. The charge/mass ratio of alpha-radiation, calculated from its deflection in superimposed magnetic and electric fields, is about 4.81×10^3 e.m. units (Rutherford, 1903) and the charge, measured by allowing the radiation to pass through an aperture of known dimensions on to an electrometer plate (see below) and assuming spherically symmetrical emission, is about 9.3×10^{-10} e.s. unit. Alpha-radiation must thus be regarded as consisting of particles, each of which is equivalent to a doubly charged helium atom (*i.e.*, He^{++}). This identity has been proved experimentally by Rutherford and Royds (1909).

The velocity and range of the alpha-particles in air depend upon the radio-element from which they are emitted, but are related to each other by the equation

$$v_0^3 = kR \quad \text{(H. Geiger, 1910)}$$

where v_0 is the initial velocity (in cm./sec.), R the range (in cms.) and k a constant having a numerical value of about 1.0×10^{27}. R itself depends, as expected, upon the medium through which the alpha-particles pass; in general, it is approximately inversely proportional to the square of the atomic weights of the media when these are reduced to constant density.

The ionising power of alpha-particles has been used to make their tracks visible in a cloud chamber (C. T. R. Wilson, 1911).

The second type of radiation emitted by radioactive substances, known as beta-radiation (Rutherford, 1899), consists of high-velocity electrons with a charge/mass ratio (at low velocities) of 1.77×10^7 e.m. units. The effective mass varies, as with all electrons, with their speed. In general, velocities of beta-particles approach the speed of light; an average value is about 2×10^{10} cm./sec., but actual velocities may vary over a wide range even when the particles are emitted by the same source. The highest velocities so far reported, about 0.99 times the velocity of light, have been observed with particles emitted by Radium-C (see below).

In a magnetic field, beta-particles are very strongly deflected from their paths.

The penetrating power of beta-particles is usually very considerable, but no range can be assigned to them since they are very easily deflected by atoms of the media through which they pass. In practice, beta-particles can be completely stopped by 3 mm. of aluminium and proportionate thicknesses of other metals.

The third type of radiation is known as gamma-radiation and was discovered by P. Curie and, independently, by P. Villard (1900). This is the most penetrating radiation of the three, is completely unaffected by a magnetic field, and is believed to consist of electro-magnetic radiations analogous to X-rays (or "Roentgen rays"). The wave-lengths of gamma-rays are, however, generally lower than those of X-rays, and vary between 10^{-8} and 10^{-11} cm. (E. Rutherford and E. N. da C. Andrade, 1914). A notable feature of gamma-radiation is that it produces secondary electrons in its passage through matter.

It is probable that the emission of gamma-rays accompanies most, if not all, radioactive processes, but the rays are not always observed. According to L. Meitner, moreover, gamma-rays are produced subsequent to, and not simultaneously with, the emission of alpha- and beta-particles.

A fourth type of radiation, commonly known as delta radiation, is unimportant in practice; it appears to be due to recoiling atoms of the radioactive substance after ejection of alpha-particles.

Theory of Radioactivity.—In order to account for these observations, E. Rutherford and F. Soddy (1903) advanced the view that radioactivity was due to the spontaneous disintegration of heavy atoms to form new elements. Reference to an actual example will make this postulate clear.

Uranium has an atomic weight of 238.2 (or a mass number[1] of 238) and disintegrates with emission of alpha-particles which, as doubly charge helium atoms, have a mass number of 4. Consequently, if each disintegrating uranium atom emits one alpha-particle only, the residual atom should possess a mass number of 234 and thus possess somewhat different physical properties. Chemical properties, which are determined by the number of extra-nuclear electrons, should also change, since the removal of two positive charges from the nucleus must be followed by removal of two extra-nuclear electrons if the resultant atom is to be electrically neutral. Such an element, now known as Uranium–X_1, has in fact been isolated from uranium; its chemical properties closely resemble those of thorium.

An important point, however, is that the product of one radioactive disintegration can itself still be radioactive and decay further. We thus arrive at the concept of a **radioactive series.** For example, it is known that Uranium–X_1 will emit beta-particles and form Uranium–X_2 (with mass number 234); that Uranium–X_2 will emit further beta-particles and form Uranium–II (also with mass number 234); and that Uranium–II will disintegrate via Ionium, Radium, Radon, etc., to a non-radioactive stable end-product (Radium–G) with a mass number of 206.

Three such series, referred to as the uranium-, actinum-, and thorium-series, since they start with these elements, are known; these are shown in Table I. together with the radiations emitted by the individual members of the series and their mass and atomic numbers. The latter give the serial position of the element in the Periodic Table and hence the total number of extra-nuclear electrons. Mass numbers in parentheses denote estimates arrived at from the mass number of the preceding number in the series and the radiation emitted by this.

Radioactive Constants.—Measurements of the activity of a radio-element over a period of time show that the rate of disintegration follows an exponential law of the form

$$I = I_0 e^{-Lt}$$

where I is the activity at time t, I_0 the activity at $t = 0$, and L a constant known as the **radioactive constant.** Since the disintegration process as a whole is a random process, this means that the activity at any one instant is proportional to the number of atoms that have not yet disintegrated.

The reciprocal of the radioactive constant, $1/L$, gives the *average life period* of the atoms of a radio-element.

In practice, it is customary to determine the so-called *half-life period* of a radio-element, *i.e.*, the time that elapses before the activity of the element falls to half its value at any one instant. Mathematically this amounts to writing the exponential decay law in the form

$$0.5\ I_0 = I_0 e^{-Lt'}$$

where t' is the half-life period. It then follows that

$$t' = \log_e 2/L = 0.693/L$$

t' has thus been found to vary between 10^{-11} second (for Thorium–C″) to 10^{10} years (for Thorium).

Position of Radio-elements in Periodic Table.—The existence of radioactive series directs attention to two points of theoretical and practical importance.

The first is that the emission of alpha- or beta-particles from a radio-element results in regular shifts of the atomic number of the element (*i.e.*, its position in the Periodic Table) to lower or higher values respectively. This regularity is

---

[1] The mass number equals the number of protons and neutrons in the atomic nucleus.

TABLE I.—THE RADIOACTIVE SERIES

The Uranium Series

Element.	Symbol.	At. Wt.	At. No.	Rays.	Half-life period.
Uranium I	U_1	238.2	92	α	4.5 × 10⁹ yrs.
Uranium-X_1	UX_1	(234)	90	β	24.5 days
Uranium-X_2*	UX_2	(234)	91	β	1.14 mins.
Uranium II	U_{11}	(234)	92	α	2.7 × 10⁵ yrs.
Ionium	Io	(230)	90	α	8.3 × 10⁴ yrs.
Radium	Ra	226.05	88	α	1,590 yrs.
Radon (Emanation)	Rn	222	86	α	3.82 days
Radium-A	RaA	(218)	84	α	3.05 mins.
Radium-B	RaB	(214)	82	β	26.8 mins.
Radium-C	RaC	(214)	83	β and α	19.7 mins.
99.96% | 0.04%					
Radium-C′	RaC′	(214)	84	α	1.5 × 10⁻⁴ secs.
Radium-C″	RaC″	(210)	84	β	1.32 mins.
Radium-D	RaD	(210)	82	β	22 yrs.
Radium-E	RaE	(210)	83	β	5.0 days
Radium-F (Polonium)	RaF	(210)	84	α	140 days
Radium-G (Uranium lead)	RaG	206	82	...	...

The Actinium Series

Element.	Symbol.	At. Wt.	At. No.	Rays.	Half-life period.
Protoactinium †	Pa	(231)	91	α	3.2 × 10⁴ yrs.
Actinium	Ac	(227)	89	β	13.5 yrs.
Radioactinium	RaAc	(227)	90	α	18.9 days
Actinium-X	AcX	(223)	88	α	11.2 days
Actinon (Emanation)	An	(219)	86	α	3.92 secs.
Actinium A	AcA	(215)	84	α	1.83 × 10⁻³ secs.
Actinium B	AcB	(211)	82	β	36 mins.
Actinium-C	AcC	(211)	83	β and α	2.16 mins.
99.84% | 0.16%					
Actin. C′	AcC′	(211)	84	α	5 × 10⁻³ secs.
Actin.-C″	AcC″	(207)	81	β	4.76 min.
Actinium D	AcD	(207)	82	...	...

The Thorium Series

Element.	Symbol.	At. Wt.	At. No.	Rays.	Half-life period.
Thorium	Th	232.12	90	α	1.39 × 10¹⁰ yrs.
Mesothorium 1	$MsTh_1$	(228)	88	β	6.7 yrs.
Mesothorium 2	$MsTh_2$	(228)	89	β	6.13 hrs.
Radiothorium	RaTh	(228)	90	α	1.90 yrs.
Thorium-X	ThX	(224)	88	α	3.64 days
Thoron (Emanation)	Tn	(220)	86	α	54.5 secs.
Thorium-A	ThA	(216)	84	α	0.16 sec.
Thorium-B	ThB	(212)	82	β	10.6 hrs.
Thorium-C	ThC	(212)	83	β and α	60.5 mins.
65% | 35%					
Thorium-C′	ThC′	(212)	84	α	3 × 10⁻⁷ secs.
Thorium-C″	ThC″	(208)	81	β	3.1 mins.
Thorium-D	ThD	208	82	...	...

---

* Possibly undergoes a branched transition, forming Uranium Z by internal conversion; this disintegrates as follows: UZ (234, 91, β, 6.7 hrs.) Uranium II

† Possibly preceded by Actino-uranium, AcU (..., 92, α, [illegible] × 10⁸ yrs.) Uranium Y (UY, 231, 90, β, 24.6 hrs.) Protoactinium

summarised in the so-called **group displacement law** formulated by K. Fajans, A. S. Russel, and F. Soddy (1913). The emission of an alpha-particle results in a product whose atomic number is two less than that of the starting substance; the emission of a β-particle results in a product whose atomic number is *one greater*.

The simultaneous or successive emission of one α- and two β-particles thus brings a radio-element back to its original atomic number even though its atomic weight has been reduced by 4 units (due to emission of the α-particle.)

The second point relates to the existence of several radio-elements having the same atomic number and hence occupying the same position in the Periodic Table. These elements, which are chemically inseparable, are said to be **isotopic** with each other. Thus, Radium–B, Radium–D, Radium–G (lead), Actinium–B and Actinium–D and Thorium–B and D are all isotopes of one another since they all have an atomic number of 82. Similarly, Radium–C and E, Actinium–C and Thorium–C form an isotope series with atomic number 83.

The separation of isotopes by physical methods will be discussed below. Here it need only be emphasised that isotopes are not confined to radio-elements, and that most elements must be regarded as a mixture of isotopes. The exceptions, *i.e.*, elements apparently not possessing stable isotopes, are elements with atomic numbers 43, 61, 85, and 87. This fact explains why the measured atomic weights of elements are unlike those of the pure isotopes—not whole numbers (*i.e.*, simple multiples of the weight of a proton) as required by modern atomic theory.

Induced Radioactivity.—Although natural radioactivity is confined to some forty elements, it has more recently been demonstrated that it can be artificially induced in a large number of comparatively stable (*i.e.*, inactive) elements by bombardment with γ-rays or fundamental particles. The mechanism involved in this transformation involves the emission of either a proton (H^+) or a neutron and positron (*i.e.*, neutral proton and positively charged electron), and leads either to the formation of a radioactive isotope of the parent element or to an actual transmutation of the parent element. An example of transmutation is provided by the bombardment of Magnesium (at. wt. 24; at. no. 12) with α-particles; this results in the production of radio-silicon (at. wt. 27; at. no. 14) and the loss of a neutron:

$$^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{27}_{14}\mathrm{Si} + {}^{1}_{0}n$$

and is followed by the subsequent radioactive disintegration of $^{27}_{14}\mathrm{Si}$ to form a stable aluminium isotope (at. wt. 27; at. no. 13).

$$^{27}_{14}\mathrm{Si} \longrightarrow {}^{27}_{13}\mathrm{Al} + {}^{0}_{1}e^+$$

where $^{0}_{1}e^+$ denotes a positron.

An example of *radio-isotope* formation (*i.e.*, reaction *without* transmutation) is provided by Potassium (at. wt. 39; at. no. 19) which, when bombarded by neutrons, yields radio-potassium (at. wt. 38; at. no. 19) and two neutrons per K atom taking part in the reaction

$$^{39}_{19}\mathrm{K} + {}^{1}_{0}n \longrightarrow 2\,{}^{1}_{0}n + {}^{38}_{19}\mathrm{K}$$

Like radio-silicon, radio-potassium will then disintegrate further by emitting positrons and yielding Argon (at. wt. 38; at. no. 18).

$$ {}^{38}_{19}\mathrm{K} \longrightarrow {}^{38}_{18}\mathrm{A} + {}^{0}_{1}e^{+} $$

In general it is now known that radioactive properties can be induced by bombardment with (1) α-particles, (2) protons, (3) deuterons, *i.e.*, fundamental particles carrying unit positive charge but possessing twice the mass of a proton and forming the nucleus of the deuterium atom, an isotope of hydrogen, (4) neutrons, and (5) γ-rays.

Bombardment with α-particles causes emission of protons or neutrons from the parent element and the formation of radioactive substances which usually disintegrate further with emission of positrons. Thus,

$$ {}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{1}_{0}n + {}^{30}_{15}\mathrm{P}; $$

$$ {}^{30}_{15}\mathrm{P} \longrightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{1}e^{+} $$

Bombardment with protons appears to form radio-elements only when involving the subsequent emission of neutrons or γ-rays; bombardment followed by emission of deuterons or α-particles result invariably in inactive products.

Bombardment with deuterons (especially fast deuterons) causes emission of protons or α-particles and yields radio-elements which disintegrate with emission of either β-particles or positrons.

Bombardment with neutrons usually only leads to radio-elements when the neutrons have been slowed down by passage through water or paraffin wax (E. Fermi *et. al.*, 1935). It will then result in emission of α-particles, protons, γ-rays or neutrons (2 per atom) from the parent element and yield products which subsequently lose electrons or positrons.

Bombardment with γ-rays invariably causes loss of neutrons and the formation of radio-elements which subsequently emit positrons. A typical example is the reaction

$$ {}^{31}_{15}\mathrm{P} + \gamma \longrightarrow {}^{1}_{0}n + {}^{30}_{15}\mathrm{P} $$

$$ {}^{30}_{15}\mathrm{P} \longrightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{1}e^{+} $$

The Measurement of Radioactive Intensity.—The strength of a radioactive body, *i.e.*, the intensity of its radioactive emission, is normally measured by its alpha- or gamma-ray activity, and referred to the alpha-ray activity of 1 gm. of metallic radium or the gamma-ray activity of the quantity of Ra C *in equilibrium* with 1 gm. of metallic radium. Measurements of radioactive intensities can thus be reduced to relatively simple counting operations, and the results expressed in terms of the "curie", *i.e.*, the number of alpha-particles emitted by 1 gm. of radium per second.

The simplest device available for this purpose is the **electroscope.** A typical design is shown in Fig. 1. Its main part is a metal rod (mounted in a good electrical insulator, such as sulphur, and hanging into a metal canister) and, attached to the top end of the rod, a strip of thin gold foil.

When the rod is charged, the foil rises (due to the repulsion of the equal charges on it and the rod) to a position depending upon the strength of the charge; there it will remain as long as no discharging occurs. If, however, alpha- or gamma-rays enter the chamber, the rod is gradually discharged by the ionisation of the ambient air, and the foil returns slowly to its original position. Since the rate of discharge under such conditions is proportional to the amount of radiation received by the electroscope, the emission intensity can be determined by assuming spherically symmetrical emission and following the position of the gold foil with a low-power microscope and a stop-watch.

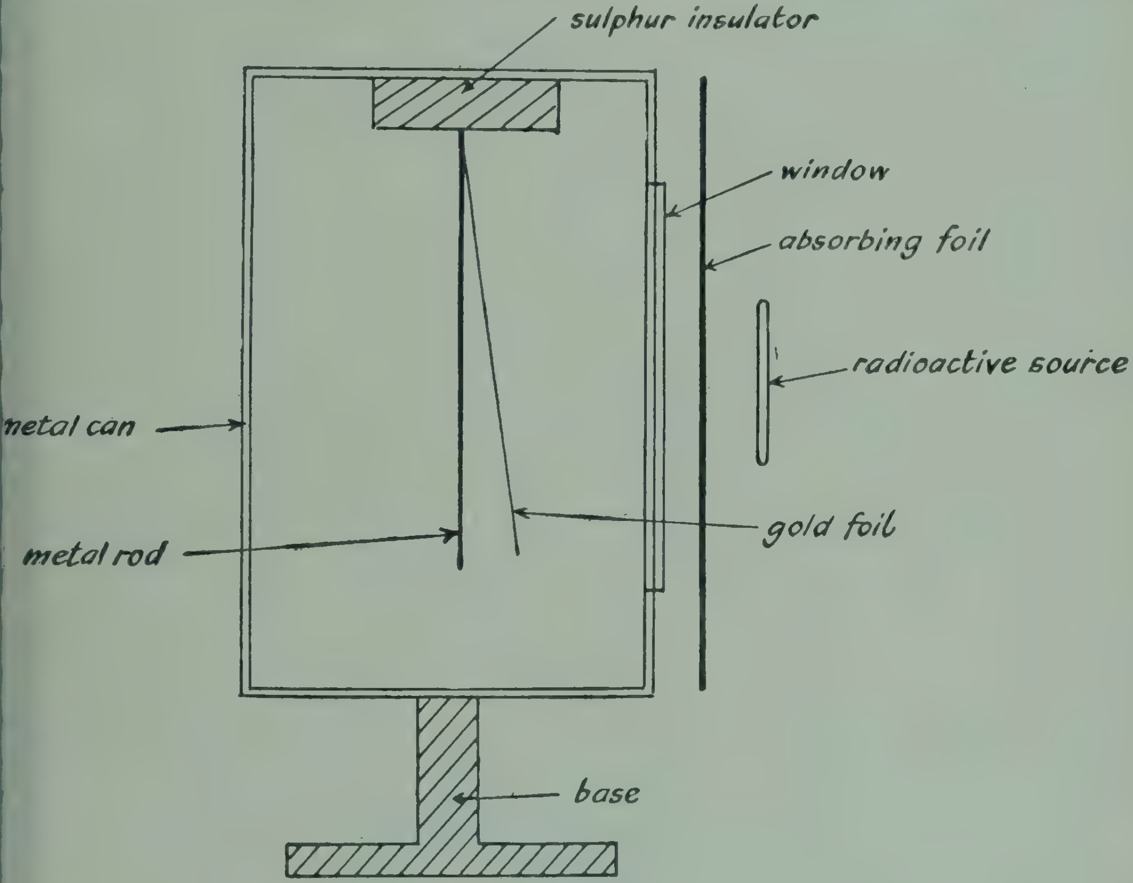


FIG. 1.—Electroscope.

More quantitative information, and particularly an *analysis* of the radiation entering the electroscope, can be obtained by varying the experimental conditions. For example, if the electroscope contains a "window" of very thin aluminium foil, *all* radiation can enter the instrument, and the *total* activity can be determined. By interposing a sheet of paper between the radioactive source and the electroscope, alpha-radiation is stopped, and the corresponding decrease in the discharge rate gives the proportion of alpha-rays. The proportion of beta-rays can be obtained in a similar manner by interposing a $\frac{1}{16}$ in. brass sheet.

An important drawback of the electroscope, however, is its rather limited sensitivity. Thus, in order to produce a visible shift of the gold foil, at least 100 alpha-particles (and an even larger number of beta-particles) must be received.

Electroscopes can therefore only be used with very strongly emitting substances. During the past decade or so, intensity measurements have consequently more and more come to be based on amplified valve counters. Two of these instruments, the **proportional amplifier** and the **Geiger-Mueller counter** are described below because of their importance and flexibility.

The **proportional amplifier** is the outcome of pioneering work carried out by Wynn-Williams in England and by Ortner and Stetter in Austria. The input end of the amplifier is an ionisation chamber (such as that shown in sectional view in Fig. 2). This consists of a collecting electrode (of plate or rod form) which is connected to the input of the amplifier, and a high-voltage electrode which is connected to a battery capable of yielding at least a few hundred volts. When radioactive radiation enters the chamber, the ions produced by it are propelled to the corresponding (positive or negative) electrode by the high-voltage electrode, and a brief current pulse (representing the flow of the ions) generated. This pulse is registered by the collecting electrode, transmitted to the input grid of the amplifier, and finally magnified. To record the pulses, one can either connect a loudspeaker to the output end of the amplifier and count the sharp cracks corresponding to the individual particles entering the ionisation chamber, or use an automatic registering device, such as is employed in telephone exchanges to register the number of calls made by a client during the counting period. These counters can be set in such a way as to record only pulses above a desired size; repeated counts with different settings can thus yield information about the character as well as the number of particles passing through the ionisation chamber.

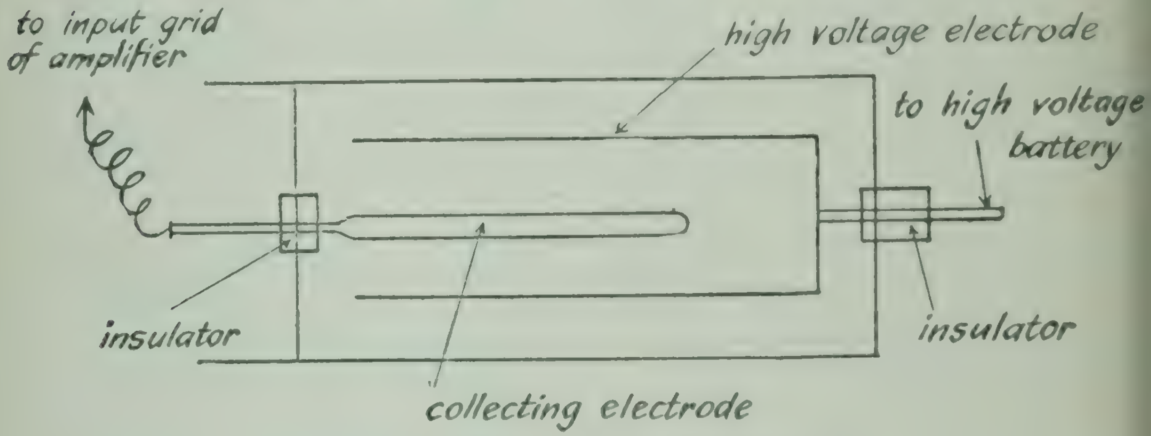


FIG. 2.—Ionisation Chamber—Sectional view.

However, since a particle emitted from a radioactive source must normally create several hundred ions in order to produce a detectable signal, it is now customary to carry out counts in a modified instrument which makes use of a phenomenon known as **gas multiplication.**

If an electric field in the ionisation chamber is made strong enough, the ions produced in it by radioactive radiation can be accelerated to such an extent that they themselves become capable of ionising gas. In this way, an avalanche reaction can be induced, and the pulse imparted to the collecting electrode multiplied to any desired level.

In practice, this effect is made use of by making the collecting electrode of the ionisation chamber of thin wire and surrounding this with a cylindrical high-voltage electrode connected to a 1,000-volt battery. The remainder of the circuit is the same as that described above (see Fig. 3).

By careful adjustment of the voltage, multiplication factors of up to about 1,000 can be obtained without seriously deviating from the proportionality between pulses and initial ionisation. With increasing voltage, however, multiplication rises very rapidly and eventually gets out of control; in other words, a single ion will then set off a discharge involving many million of ions.

This difficulty has been overcome in the **Geiger-Mueller counter** by quenching the discharge by (*a*) filling the counter with a special gas mixture (*e.g.*, argon with a trace of alcohol), (*b*) increasing the resistance R in Fig. 3 to beyond 1,000 megohms,[1] or (*c*) making the amplifier reduce the voltage on the counter for a fraction of a second after receipt of the pulse. Since an ionising particle produces all its ions practically instantaneously, each particle passing through a Geiger-Mueller counter will produce one pulse only and the counter is immediately ready to receive another particle.

In general, a Geiger-Mueller counter will record accurately up to about 10,000 pulses per minute.

It may also be noted that where very high counting rates are desirable or necessary, it is expedient to use a "scale of two" device in which only *every alternate* pulse is transmitted to the counter. Thus, if six "scales of two" are used, the counter records only every sixty-fourth pulse, and a very high resolution is achieved.

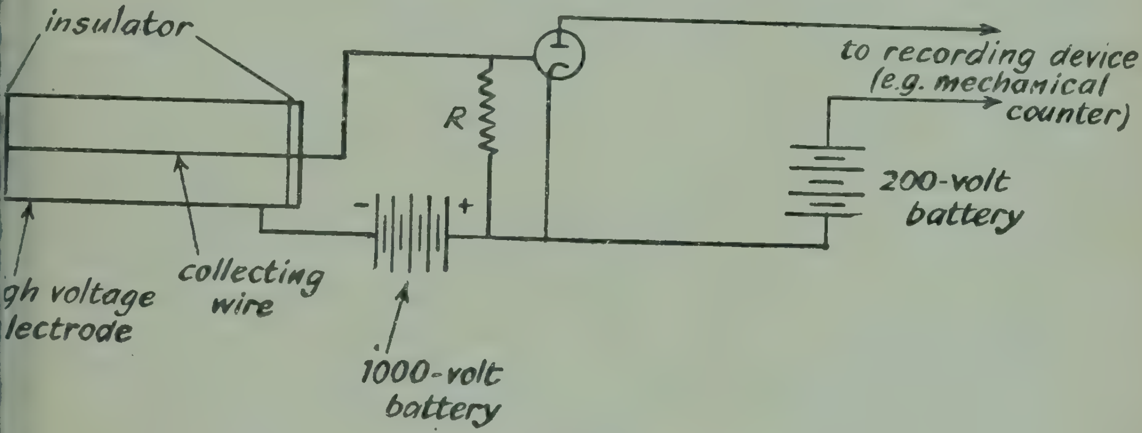


FIG. 3.—Geiger-Mueller Counter with recording circuit.

Separation of Radio-elements: I. Chemical Methods

Extraction and purification methods appropriate for the isolation of radio-elements are almost without exception complicated by the marked chemical similarity which these elements display towards each other and towards certain non-radioactive elements. For example, in order to free radium from associated barium P. and M. Curie had to resort to some 2,000 fractional recrystallisations of the mixed chlorides (or bromides). The following account is therefore only intended to provide *examples* of separation methods.

(*a*) **Separation of Radium.**—The source material is normally pitchblende or carnotite (*cf.*, Section LXXXIII, Uranium). After dressing to remove gangue and other associated impurities, this is dissolved in some suitable mineral acid (*e.g.*, carnotite in hydrochloric acid), and all elements forming more or less insoluble sulphates precipitated with a mixture of barium chloride and sodium sulphate. The sulphates, which contain radium and barium in almost quantitative amounts, are then converted into the carbonates by vigorous boiling with a solution of sodium carbonate, the carbonates re-dissolved in pure hydrochloric acid, and the solution treated with sulphuric acid. This process is repeated until all iron, lead[2] and calcium (normally associated with the ore) are completely removed. In the final step, the radium-barium concentrate is converted into the chlorides and radium separated by fractional recrystallisation. It may be noted that, whilst this operation can be speeded up by using bromides, recent practice has reverted to the fractionation of the chlorides, which are rather more stable.

---

[1] This method is now little used as the counter usually takes too long to recover after a pulse.

[2] In modern plants, such as those situated at Port Hope, Ontario, and at Great Bear Lake, ead is removed by treating the sulphate precipitate with brine and extracting the lead chloride hus formed with hot water.

It is estimated that this process yields about 80 per cent. of the radium initially present in the ore.

In a modified extraction process, known as the Ulzer-Somner process, the procedure is as follows: The source material is boiled for some hours with concentrated sulphuric acid, or fused with acid sulphates, and the residue obtained after repeatedly extracting the product with water is boiled, under pressure, with caustic alkalies or alkali carbonates. The precipitate is then again extracted with water and finally boiled with pure dilute sulphuric acid. The barium-radium concentrate is thus obtained as an insoluble residue which can be resolved, as before, by fractional recrystallisation.

According to a recommendation by F. Soddy, the lengthy wet extraction process can in many cases be replaced by reduction of the insoluble sulphates to the sulphides in a current of coal gas, and by final dissolution of the products in acid.

A similar short-cut has been suggested by Ebler and Bender (*Zeitschr. anorg. Chem.*, **83**, 149, 1913). The dry, powdered crude sulphates of Ra, Ba, etc., are reduced to sulphides by mixing them with calcium hydride, pressing the mix into a crucible and kindling as in the Thermit process. The reaction is then as follows:

$$RaSO_4 + 4CaH_2 = RaS + 4CaO + 4H_2.$$

The reaction product is then cooled, powdered, quickly dissolved in hot dilute hydrochloric acid and boiled to expel hydrogen sulphide. Any lead present remains undissolved as PbS, and silica also remains undissolved. The radium is then separated from the filtrate by evaporation to dryness and treating the residue with HCl gas until about 75 per cent. of the barium is deposited. A total recovery of 75–80 per cent. of the original radium content is claimed. It should be pointed out, however, that the method has been criticised on the grounds of high cost of calcium hydride and the rapid re-oxidation of the sulphides.

Among proposed modifications relating to the fractionation of the radium-barium concentrate, an old German patent (No. 264,901, 1912) is of interest: according to this, the separation can be made more efficient by using such salts as picrates, bromates, and ferrocyanides. As solvents, ethyl alcohol and acetic acid are recommended.

(*b*) **Separation of Ionium.** As the parent substance of radium, ionium occurs in all minerals that contain uranium and radium. Chemically, however, it resembles thorium, and it can therefore be isolated from, say a uranium ore, by fractionating the rare earths-concentrate and purifying the thorium fraction of this concentrate. (In this connection, see Section LXXVII, Thorium.)

It is, however, important to note that ionium cannot be separated from thorium, and that pure ionium can therefore, theoretically, only be made from starting materials that are completely free from thorium. (It is possible that isotope separation methods may find some use here, but so far the demand for ionium has not been sufficient to justify this approach.)

(*c*) **Separation of Polonium.**—Separation of this element, which is the missing top member of group VI B of the Periodic classification, is based on the close chemical similarity between it and bismuth. Thus, M. Curie separated polonium from the bismuth oxychloride fraction of pitchblende by

i. fractional precipitation of the basic nitrates with water,
ii. fractional precipitation from strong hydrochloric acid solutions, and
iii. sublimation *in vacuo*.

According to Marckwald, polonium can also be separated from bismuth and other associated impurities by dissolving the entire concentrate in hydrochloric acid, and immersing a copper or silver plate in the solution; polonium collects on such a plate in practically quantitative amounts.

The chemical similarity between polonium and tellurium can also be used to separate the former. If a small quantity of stannous chloride is added to a solution of the bismuth concentrate in hydrochloride acid, polonium and tellurium are precipitated, and from this mixture polonium can be isolated by dissolving in dilute acid, adding hydrazine hydrate (to precipitate tellurium), and finally precipitating polonium with a further quantity of stannous chloride.

When polonium is to be separated from **radiolead** (a mixture of radium–D, radium–E, polonium and lead), the following procedure can be used. The radiolead is dissolved in nitric acid and the solution evaporated until, on cooling, some of the lead nitrate crystallises out. This operation is repeated until only a trace of lead remains in the polonium fraction. The solution is then evaporated to dryness, the residue re-dissolved in a minimum of hot water, and a clean copper plate (varnished on one side with Brunswick black or some similar material) rotated in the solution. Polonium will be deposited on the plate, and up to 95 per cent. of the polonium initially present in the fraction can thus be removed.

(*d*) **Separation of Mesothorium.**—The chemical properties of mesothorium are identical with those of radium, and the metal can therefore be isolated from a mesothorium concentrate by adding a little barium chloride to the solution, precipitating the insoluble sulphate with sulphuric acid, and fractionating the mesothorium-barium concentrate in exactly the same way as the radium-barium concentrate.

Suitable source materials are all thorium-bearing minerals (*cf.*, Section LXXVII, Thorium). It should, however, be noted that mesothorium preparations tend to be rather unstable, as the half-life period of mesothorium is only about 5·5 years.

(*e*) **Separation of Radiothorium.**—Radiothorium, another important radioactive constituent of thorium minerals, cannot be directly separated from such minerals because of its chemical identity with thorium. It can, however, be obtained from mesothorium, of which it is a degradation product. The procedure is as follows: The old mesothorium preparation is dissolved in a little hydrochloric acid, and to this solution is added a dilute solution of aluminium nitrate (or of any substance precipitated by ammonia). The mixture is then treated with gaseous ammonia, and aluminium and radiothorium precipitated; any mesothorium and radium present remain in solution. Finally, the aluminium-radiothorium concentrate is fractionated by recrystallisation.

Radiothorium loses its activity even more quickly than mesothorium; thus, after ten years, only about 3 per cent. of the original quantity is left.

It may also be pointed out that radiothorium provides a suitable source of Thorium–X, which is formed from radiothorium by emission of an alpha-particle. This substance, which is chemically identical with radium and mesothorium, is isolated by dissolving the radiothorium preparation in acid, and passing ammonia gas through the solution until all residual radiothorium is precipitated. Thorium–X remains in solution.

Other preparations can be obtained by analogous methods. For example, radioactinium is isotopic with thorium and ionium, and can therefore be isolated from any thorium-actinium concentrate in exactly the same way as radiothorium. Similarly, Actinium–X is isotopic with radium, mesothorium and Thorium–X, and can be isolated from a radioactinium preparation (from which it is formed by emission of one alpha-particle) in the same way as Thorium–X from radiothorium.

Separation of Radio-elements. II. Separation of Isotopes

Attention has already been drawn above to the existence of several isotopic radio-elements, *i.e.*, elements with the same atomic number and hence occupying the same position in the Periodic Table. These elements (like non-radioactive isotopic elements) possess almost, though not quite, identical chemical properties, and can therefore in general only be separated by physical methods based upon the small differences in their respective atomic weights.

The earliest work on isotopes was carried out in England by F. W. Aston (1927 *et seq.*) with the aid of the mass spectograph: for an account of this work the reader is referred to Aston's book. Here it is only possible to indicate the methods that have found use in large-scale isotope separation.

The first successful separation on a commercial scale was achieved with hydrogen which contains the isotope *deuterium* (mass number 2) to the extent of about 0.05 per cent. Because of the greater "zero-point energy" of hydrogen in H_2O, it was found that water is somewhat less stable than the isotopic compound D_2O (deuterium oxide or "heavy water"), and Urey and Washburn (1932) showed that this meant that when water is electrolysed, the undecomposed fraction is progressively enriched with D_2O. By using 20 litres of water from an old electrolytic cell, it was thus possible to isolate about 0.5 c.c. containing about 70 per cent. D_2O (Lewis and MacDonald, 1933).[1]

Hydrogen-Deuterium mixtures, however, represent the simplest separation problem; in general, differences in the atomic weights of isotopes contained in an isotopic mixture are very much smaller, and separation methods correspondingly more involved (and less efficient).

Broadly speaking, modern separation methods fall naturally into two classes, the first covering diffusion methods, and the second techniques based upon evaporation and distillation.

By Graham's diffusion law, the rate of diffusion of a gas is inversely proportional to the square root of its density (or molecular or atomic weight), and it follows therefore that the atoms or molecules of a light isotope will diffuse through a porous membrane more rapidly than those of a heavy isotope. Based on this principle, Hertz (1932) has developed a separation method which has proved extremely efficient: using a system of 24 diffusion pumps arranged in a "cascade" pattern, he was thus able to separate a neon fraction containing about 70 per cent. of the isotope of mass number 22 (*i.e.*, ^{22}Ne); the original sample contained only 10 per cent. of this isotope. By the same technique, it has proved possible to isolate a methane fraction containing about 50 per cent. of the ^{13}C isotope.

A major disadvantage of Hertz's method is, however, that it can only handle relatively small quantities (since the diffusion pumps can only work at low pressures). The thermal diffusion method described by Clusius and Dickel (1938) is therefore likely to prove of more general usefulness. The isotope is here introduced into the annular space between two concentric tubes (or a tube and coaxial wire) and the inner tube or wire heated electrically to about 500° C. As a result of thermal diffusion, the heavier isotope tends to concentrate along the cool outer tube, and, since thermal syphoning also causes the gas to rise along the hot surface and to flow down the cold, it is also found in greater proportion near the bottom of the apparatus. The method has been claimed to effect a rapid and efficient separation of the isotopes of neon, carbon, argon, and chlorine, and it is of interest to note that it has still more recently been used to separate uranium isotopes from *liquid* uranium hexafluoride (Abelson, 1942–3). Whether it can be applied to other liquids is, however, doubtful.

Evaporation and distillation methods depend upon the fact that the rates at which otherwise identical atoms or molecules evaporate from a given surface are inversely proportional to the square roots of their masses. If the evaporating molecules are immediately condensed (and in this way prevented from returning to the surface from which they originate), the distillate will therefore become enriched in the lighter isotopes. This principle was first applied by Bronsted and Hevesy (1920–22) to the separation of the isotopes of mercury. The mixture was evaporated at 40°–60° C. in a high vacuum and the distillate condensed on a plate suspended about 1 cm. above the surface of the mercury and cooled in liquid air. The same method has subsequently been used to effect a partial separation of the isotopes of potassium (Hevesy, 1927) and of zinc (Egerton, 1927).

---

[1] It may be noted that this method still forms the basis of commercial production of heavy water. For uses of this substances, see section on Nuclear Energy.

Distillation methods with efficient rectifying columns were first employed by Keesom and Dijk (1932) in order to separate neon isotopes at liquid air temperatures; the extreme fractions obtained by these investigators had atomic weights of 20.14 and 20.23 respectively; the atomic weight of ordinary neon is 20.18. Partial separation of nitrogen isotopes by distillation of liquid ammonia, and of oxygen isotopes by distillation of water, has also been reported.

During recent years, some attempts have also been made to separate isotopes by methods based on slight differences in their chemical properties. Owing to their different masses, isotopic molecules react at different rates, and it has been shown that in a reversible reaction involving an exchange between two isotopic forms of a given element, the equilibrium constant departs from the simple value to be otherwise expected. For example, in the exchange reaction

$$^{16}O_2 + 2H_2{}^{18}O = {}^{18}O_2 + 2H_2{}^{16}O$$

the equilibrium constant at 25° C. was found to be 1.012; if the two isotopes of oxygen were equally reactive, the equilibrium constant would be unity. The experimental result implies therefore that the reaction leads to a gradual enrichment of the gas phase in $^{18}O_2$. Processes based upon this observation have been used by Urey *et al.* (1936 *et seq.*) in order to effect a partial separation of isotopes of nitrogen (by the interaction between NH_3 and NH_4^+), and of carbon (by the interaction between HCN and CN^-), but have not otherwise found application. Whether they will do so in the future is uncertain.

Uses of Radioactive Substances.—Prior to the second world war, the use of radioactive preparations was restricted to medicine, and in particular to the cure of **cancer**. External treatment was usually given by irradiation of the affected tissues with gamma-rays (from either radium salts, radium emanation, mesothorium, or radiothorium), and internal treatment with preparations radium emanation, or thorium–B, thorium–C and thorium–D. In the latter treatment, the physiological effects are mainly due to the emission of alpha-rays from the radioactive preparations.

The early hopes of a permanent cure of cancer by such treatment have, however, been largely unfulfilled, and though radium treatment is still used widely, it is now recognised that this can be applied only to certain forms of cancer, and that it may have several deleterious effects (such as destruction of healthy tissue under and around the cancer, and consequent inability of the wound to heal satisfactorily.

More recently, however, considerable progress has been made in various fields with the use of **radioactive tracers,** *i.e.*, relatively cheap preparations which are either naturally radioactive, or which have been made radioactive by bombardment with elementary particles (*cf.*, above) in a low energy uranium pile.[1]

The most important applications of such tracers are still in the fields of medicine and biology. In medicine, radioactive **iodine** is thus used in the treatment of certain forms of goitre and in tracing loose cancerous thyroid tissue, and **radio-sodium** (produced by deuteron-bombardment of sodium or magnesium) in tracing the extent of a gangrenous area in cases where gangrene is due to poor blood circulation. Similarly, **radio-calcium** has proved valuable in investigating arterio-sclerosis associated with the deposition of calcium in arteries; **radio-phosphorus** (included in diets) has been used in studies of the formation of caries; and radio-phosphorus and **radio-strontium** have been demonstrated to be effective in the treatment of leukæmia. The principal merit of radioactive tracers in the treatment of cancer has been that the usually short life of these tracers minimises the danger of over-exposure of the cancerous growth.

---

[1] Such a pile, known as "GLEEP," is at present in operation at Harwell Research Station.

In biology, **radio-carbon** has been used to study the fate of carbon in photosynthesis; radioactive isotopes of **nitrogen** (^{13}N) and **phosphorus** (^{32}P) have been applied to investigate the behaviour of these elements in animal and plant metabolism; and other radioactive isotopes (such as **radio-sodium, radio-iron,** and **radio-sulphur**) have been used in biological absorption studies. For example, radioactive iron has recently been used to determine the total volume of blood in dogs: by feeding it to one dog, extracting a known number of active red blood cells and then injecting these into a second dog. The dilution of these active cells is a direct measure of the blood volume in the second dog. Similarly, radioactive carbon has been used to examine the path and history of lactic acid produced in muscles by exertion. (See *Science*, **91**, 421, 1940.)

Some demand for radioactive preparations has also been created in agriculture. For example, waste products from extraction processes will almost invariably contain some radioactive materials and are therefore suitable as fertilisers; it has been claimed that the addition of such waste to ordinary fertilisers in the ratio of 1 : 10 can cause a two- and three-fold increase in crop yield per acre. More concentrated radioactive preparations are also now used to produce new plant variants by increasing the incidence of mutations by irradiation.

Finally, radioactive tracers have been used to study self diffusion of metals; wear on internal engine parts; reaction mechanisms; and analytical procedures. An example of the application of tracers to reaction mechanisms is given by the elucidation of the mechanism of the isomeric change of N-chloroacetanilide to *p*-chloroacetanilide in the presence of hydrochloric acid. Experiments with hydrochloric acid containing **radioactive chlorine** (as chloride ions) has shown that this change takes the form

$$C_6H_5NClAc + H^+ + Cl^- = C_6H_5NHAc + Cl_2;$$
$$C_6H_5NHAc + Cl_2 = p.ClC_6H_4NHAc + H^+ + Cl^-.$$

As an example of analytical applications of radioactive tracers, proof for the probable existence of bismuth hydride may be quoted; magnesium filings were coated with thorium C or radium C (both isotopic with bismuth), and dissolved in dilute hydrochloric acid. The gas evolved was radioactive, could be condensed in liquid air, and decomposed on heating, and therefore almost certainly contained bismuth hydride.

Occurrence of Radioactive Ores.—Radioactive ores occur in many of the older rock formations associated with the precious metals, gold and silver, and with the heavier metal ores and rare earths. Detection of radioactive ores in such deposits is now commonly carried out with surveying types of the Geiger-Mueller counter, portable forms of which have been developed by leading suppliers of electronic instruments in many parts of the world. Pointers towards the presence of radioactive ores in the older formations are igneous intrusions, discoloration producing "smoky" quartz, dark purple fluorite, brick red or brownish feldspars, and the bright colours of secondary uranium minerals, vivid lemon, yellow, orange, and greens.

Some of the properties of the principal uranium containing ores are summarised in the tables contained in the Sections on Thorium and Uranium, which are based on the "Abridged Table of Uranium and Thorium Minerals," published by Nucleonic and Radiological Developments Ltd.

SECTION LXXXVI

ELECTRIC FURNACE PRODUCTS INDUSTRY

By H. D. K. Drew, B.Sc. (Lond.)

Revised by Wilfrid Francis

LITERATURE

Calcium Carbide and Cyanamide.—

C. and C. H. Bingham.—"Manufacture of Carbide of Calcium." 1928.
C. Aall.—"Contribution a l'etude du carbure de calcium industriel." Paris, 1940.
C.T.J., **76**, 723 (1925); **80**, 391 (1927); **87**. 618 (1930).
A. E. Banghen.—*Can. Chem. Process. Ind.*, **28**, 805, (1944).
C.I.O.S. XXXVII–92.—German Carbide, Cyanamide, and Cyanide Industry, 1945.
F.I.A.T. 728.—Continuous Process for the Manufacture of Calcium Cyanamide.
B.I.O.S. 1046.—German Carbide and Cyanamide Industry, 1947.

Carborundum, Aloxite, and Abrasives.—

L. Wright.—*Chem. and Ind.*, **47**, 1154 (1928).
F. L. Nobes.—*Ind. Chem.*, **6**, 183 (1930).
B. Kleinschmidt.—"Schlief und Poliermittel-Kalender." Essen, 1942.
T. F. van Oss.—"Warenkennis en Technologie." Amsterdam, 1937.
H. J. Moller.—*Polytech. Weekblad.*, **36**, 261 (1942).
F. Muller and Tor Sunde.—*Die Chemie*, **56**, 355 (1943).

Graphitisation.—

Arndt and Pollack.—*B.C.A.* **B**, 134 (1932); *Chem. and Ind.*, **43**, 250 (1924).
J. H. Lausing.—*T. Am. Foundryman's Assn.*, **50**, 126 (1942).

General.—

A. Givelet.—*Mem. Soc. Ing. Civils.*, **91**, 73 (1938).
Z. Ryska.—*Strojnicky Obzor.*, **19**, 380, 407 (1939).
—— *Chem. Obzor.*, **18**, 153 (1943).
—— *Chem. Zentr.*, I, 43 (1944).
W. Finster.—*T. Am. Foundrymen's Assn.*, Preprint No. 39, 59 (1939).
G. H. S. Price *et al.*—*G.E.C. Journal*, **11**, 223 (1941).

Alundum.—

R. Schniedler.—*B.C.A.* **B**, 948 (1930).
F. Krauss.—"Synthetische Edelsteine." Berlin, 1929.
J. Papish and W. J. O'Leary.—*Ind. Eng. Chem.* An. Ed., **3**, 13 (1931).

Silicon and Ferro-Silicon.—

F. M. Becket.—*Ind. Eng. Chem.*, **16**, 197 (1924).
V. E. Vasilev and K. I. Vaschenko.—*Teoriya Prakt. Met.*, **4**, 20 (1938).
C. J. Smithells.—"Tungsten: A Treatise on its Metallurgy, Properties, and Applications." London, 1936.

Phosphorus and Ferro-Phosphorus.—

C. H. Aall.—"Chemistry and Industry." December 30, 1950.

Powder Metallurgy.—

B.I.O.S. 706.—Metal Powders (Sintered), 1946.
B.I.O.S. 1509.—Further Details of German Powder Metallurgy, 1948.
B.I.O.S. 1694.—Widia Tungsten Carbide, 1948.
F.I.A.T. 772.—German Powder Metallurgy, 1948.
W. Gowland.—"The Metallurgy of the Non-Ferrous Metals." London, 1943.
W. Hotop.—*Stahl-u-Eisen*, **61**, 1105 (1941).
Hidizi Hotta.—*Tetsu-to-Hagane*, **27**, 373 (1941).
F.I.A.T. 413.—Tungsten and Molybdenum Wire for use in Lamps and Radio Tubes, 1945.
B.I.O.S. 925.—Tungsten Carbide Research in Germany, 1946.

SILICON CARBIDE

Crystalline silicon carbide, SiC or **carborundum,**[1] was discovered accidentally, in 1891, by E. G. Acheson, whilst trying the impregnating of clay with carbon at a high temperature produced electrically.

The first corborundum furnace was that of the Carborundum Company at Monongahela in 1893; it consumed about 75 H.P., and produced 45 tons of carborundum a year. In 1895, with the formation of the Niagara Falls Power Company, much larger furnaces were constructed by the Carborundum Company at Niagara Falls; and at the present day there are many furnaces of about 2,000 H.P. in continuous operation producing nearly 60,000 tons of silicon carbide per annum.

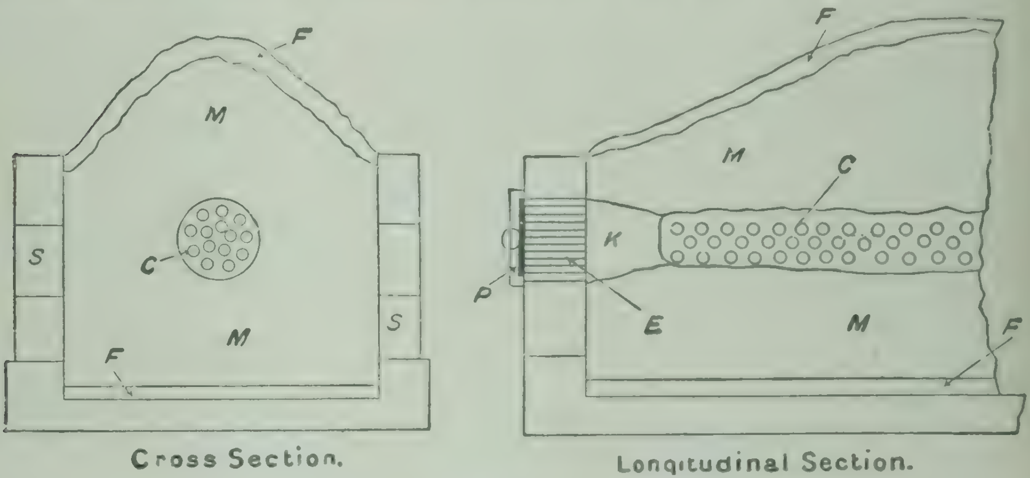


Fig. 1.—Carborundum Furnace.

Manufacture.—Carborundum is manufactured on the large scale by heating together in the electric furnace a mixture of silica, SiO_2, and carbon. The silica is usually in the form of quartz, and the carbon in the form of coke.

The formation may be expressed by the equation:—

$$3C + SiO_2 = 2CO + SiC.$$

The furnace used for the production of carborundum is of the resistance type, the size varying in different localities. Furnaces taking from 2,000–3,000 H.P. have been constructed. A carborundum furnace unit consists of five furnaces, only one at a time being in operation, while the rest are loading, unloading, or cooling.

Fig. 1 shows a modern carborundum furnace in cross section and elevation. The furnace is about 30 ft. long, 12 ft. wide, and 10 ft. deep, and has permanent end walls of concrete which contain the terminals, while the side walls S are built up of fire-bricks set in iron frames capable of ready removal by means of an electric overhead crane for discharging. The furnace ends are kept cool by a water-circulating system.

---

[1] Carborundum is the trade name for some of the silicon carbide manufactured by the Carborundum Co. and should not be applied to silicon carbide made by other firms.

The resistance core C is built about half-way up the charge. It is cylindrical, being about 3 ft. in diameter, and consists of granular coke which has become partly graphitised in a previous run. It has a slight upward curve to allow for sagging, owing to contraction of the charge during the run, and is connected at either end to the electrodes E, which consist of a number of horizontal carbon rods, by a layer of finely-powdered compressed carbon K. The electrodes are clamped to thick copper plates P connected to the cable.

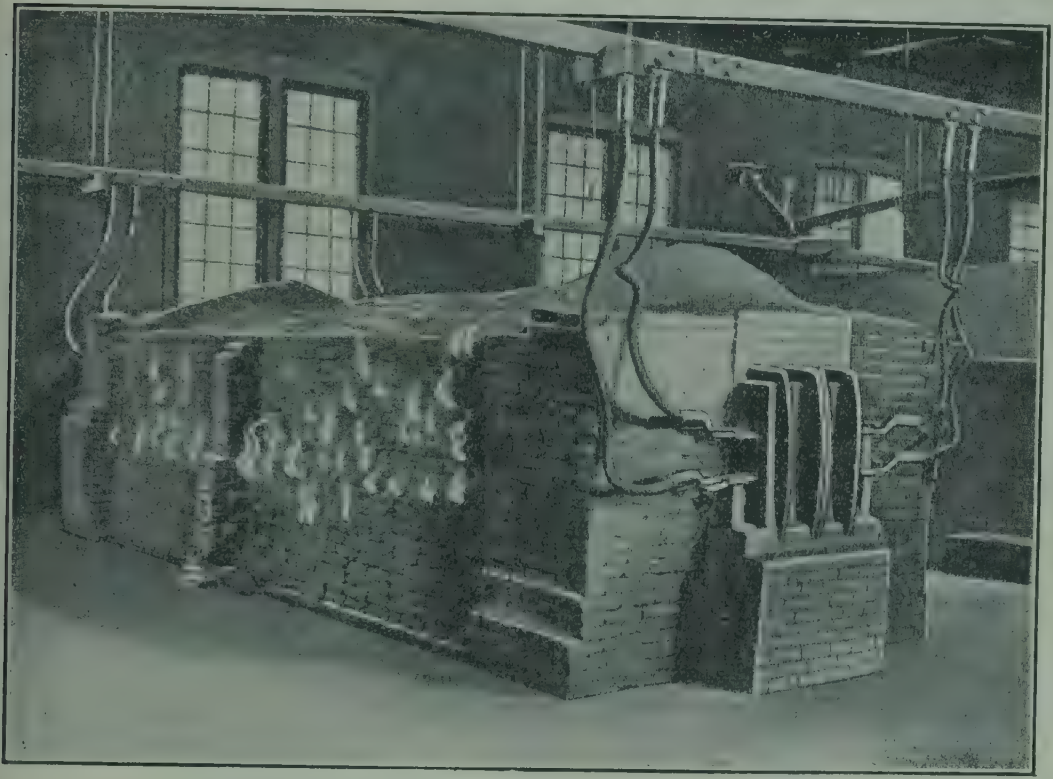


FIG. 2.—Fitz-Gerald's Carborundum Furnace in Action.

The raw material M consists of a mixture of silver sand, coke, sawdust, and salt, having the composition—

Quartz - - - - -	52.2 parts.
Coke - - - - - - -	35.4 ,,
Sawdust - - - - - -	10.6 ,,
Salt - - - - - - -	1.8 ,,

The sawdust is added in order to render the material porous, and so to aid the escape of carbon monoxide during the process of interaction between the silica and carbon. The addition of salt is found to increase the purity of the carborundum produced, since at the high temperature of the furnace it forms volatile compounds with the metallic impurities.

The mixture of dry powdered materials is fed into the furnace from an overhead conveyer, and when the furnace is loaded an alternating current is passed for thirty-six hours. At the beginning of a run the voltage is about 230 and the current about 6,000 amperes, but as the process proceeds the resistance decreases rapidly and then becomes constant, the voltage being finally about 70 and the current about 20,000 amperes. The carbon monoxide, CO, produced during the reaction, escapes at the sides and top of the furnace and burns there with a blue flame. The reactions which proceed in the furnace are very complicated, but the simple result of the formation of carborundum may be expressed by the equation given above.

When the furnace is dismantled after the run, the core is found to be surrounded by a thin layer of graphite, while next to this is a layer some 20 in. thick of crystalline carborundum, the crystals being larger nearer the core. This in turn is surrounded by a layer of "**carborundum firesand**," or so-called "amorphous carborundum," or "whitestuff." It contains oxygen and probably consists of a mixture of **siloxicon** (*q.v.*) and amorphous silicon carbide. Finally the whole is surrounded by more or less unchanged material.

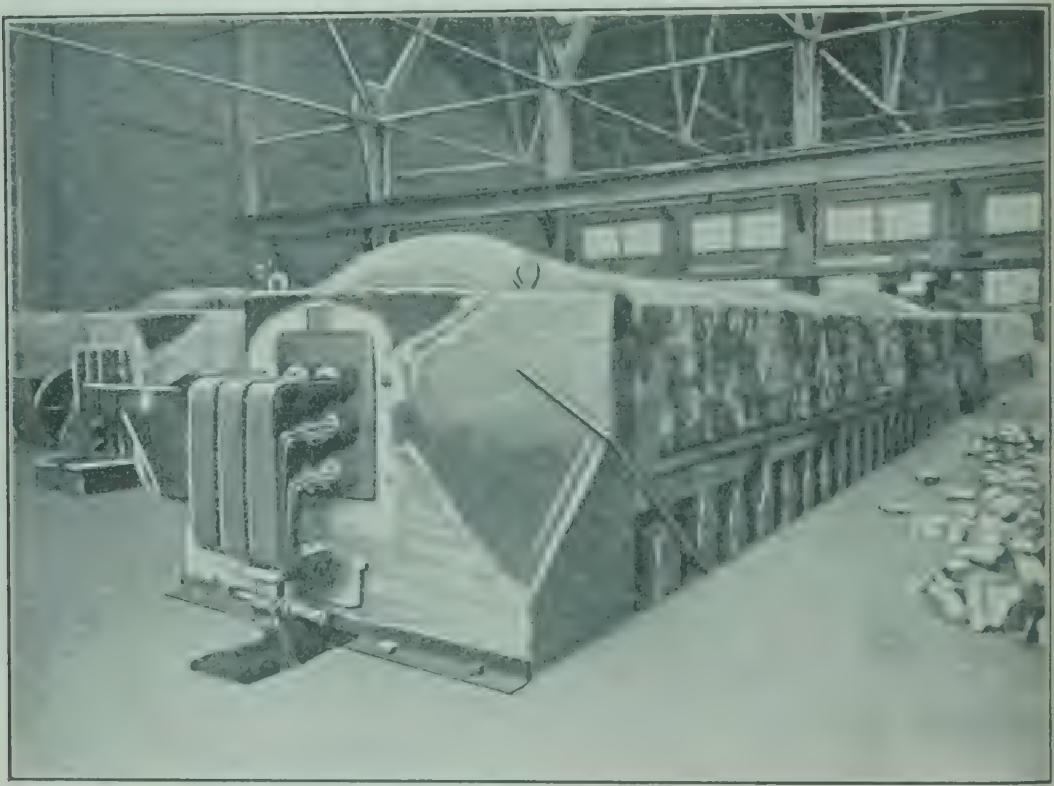


FIG. 3.—Modern Type of Carborundum Furnace used by the Carborundum Company, Niagara Falls.

The temperatures of formation of these various products are of the greatest importance, since upon them will depend the conditions for successful working. **Tucker** and **Lampen** (1906), **Gillett** (1911) and **Saunders** (1912) have all carried out determinations, with results which agree fairly well considering the difficulty of the investigation. L. E. Saunders gives the temperature of formation of crystalline carborundum as 1,840° C. ± 30° C., and of its decomposition into graphite and carbon as 2,240° ± 5°. The graphite found surrounding the core of the furnace has the skeleton form of carborundum crystals, so that we must conclude that it is produced by the decomposition of carborundum first formed, the changes taking place whilst the temperature of the core is rising from about 1,840°–2,240°. The same investigator gives the temperature of formation of firesand as 1,600° ± 50°, and of its decomposition into crystalline carborundum, of course, as 1,840° ± 30°.

The carborundum, the average yield of which is about 9 tons in each run, is transferred in large lumps to roll crushers, where it is broken up and washed. It is finally purified by treatment with sulphuric acid, washed with water, dried, and separated into grades according to degree of fineness. It is then ready for fashioning into wheels or for other employment.

Properties.—Carborundum forms masses of lustrous crystals of the hexagonal system, which, when pure, are colourless, but which, as commerically produced, vary in colour from yellow to greenish-grey or blue-black. The crystals are doubly refractive, both indices of refraction being higher than the refractive index of the diamond. Carborundum has a specific gravity of 3.123, conducts heat and electricity, and is remarkable for its extreme hardness (which is about 9.5 on the Moh's scale as against 10 for diamond), its infusibility, and great resistance to chemical change. It can be heated to a temperature of 2,240° C. (L. E. Saunders) before it breaks down, without melting, into silicon and graphite; while, if heated to whiteness in oxygen or air, it very gradually changes into carbon dioxide and silicon dioxide, becoming coated with a layer of the latter substance. It is not attacked by acids to any extent (though syrupy phosphoric acid decomposes it at 230°), but is decomposed by fused alkalis into carbon and a silicate. Chlorine slowly decomposes it at 600°; rapidly at 1,200°. It has a high thermal conductivity and a low coefficient of expansion.

Amorphous silicon carbide is not produced in the commercial furnace. The so-called "**amorphous carborundum**," or "**whitestuff**," produced during the manufacture of crystalline carborundum is a mixture of silicon carbide, with variable amounts of a variety of siloxicon (*q.v.*).

Commercial carborundum, after purification, always contains the oxides of iron, aluminium, and calcium, the total of these impurities being generally under 1 per cent.

Uses of Carborundum.—The usages to which carborundum is put are numerous. Chief among them is its employment as an abrasive (see p. 433), for which purpose it is fashioned into grindstones and wheels by mixing with some bonding material, such as kaolin or felspar, pressing into shape and igniting. In this form it is extensively used for grinding and polishing metal, porcelain, marble, granite, wood, glass, leather, precious stones, etc. It is also employed for rice hulling. The firesand is mixed with silicate of soda or fire-clay, as binding material, and used to an increasing extent as a refractory in brass, aluminium, and zinc manufacture. The residual carborundum powder obtained from the crushing mills is used in steel manufacture as a source of silicon and carbon, in place of ferrosilicon. Carborundum crystals have also been used in the receiving circuit of wireless telegraph apparatus as rectifying crystals.

Statistics.—Carborundum is manufactured, among other places, at Niagara Falls (United States of America), Chippawa (Canada), Düsseldorf-Reisholz (Germany), La Bathie (Savoy), Benateck (Bohemia), Prague (Austria), and Bodio (Turin); while a company has been projected to work on the West Coast of Scotland.

By far the greatest production of silicon carbide is in the U.S.A. and Canada. Production in these two countries during 1938 was 22,600 tons, and by 1947 production had risen to 56,900 tons.

Silundum Articles.—Both Acheson and Bölling have constructed refractory articles, such as crucibles, tubes, etc., by shaping pieces from sand and coke, or firesand and sand, and heating in an electric furnace to a high temperature; or by shaping the articles from graphite, embedding them in the charge of a carborundum furnace, and subjecting them to the action of silicon vapours at a high temperature.

The articles are said thus to become coated with a layer of carborundum, of thickness depending on the duration of heating; but in all probability the action is not simply that of the formation of carborundum, and has not yet been cleared up.

By this process the articles, while retaining their shape, become possessed of great hardness and resistivity, and are capable of conducting electricity at high temperatures. They are known to commerce as "silundum" articles, and are used for electrical cooking apparatus and other purposes.

F. G. Tone (U.S. Patent 992,668, of 16th May 1911) shaped the pieces of a mixture of carborundum and carbon, bound together with glue or other substance. He then heated them in a carborundum furnace, when combination with vapours of silica or silicon took place and the binding material was volatilised. By this means he could vary the porosity and resistance of the product. The electrical resistance of silundum is about six times that of carbon, and it is capable of standing a temperature of 1,600° for a considerable time without crystallising.

Siloxicon.—This substance is, as described above, always produced, together with silicon carbide, in the carborundum furnace in a zone of lower temperature than that in which the carborundum crystals are formed.

It contains oxygen, has a variable composition corresponding roughly with the formula Si_2C_2O, and has been said to be a mixture of silico-carbides from Si_2C_2O to Si_6C_6O. P. E. Spielmann finds that the composition would correspond with that of a mixture containing about 71 per cent. of Si_2C_2O, 11 per cent. of $SiCO_3$, 10 per cent. of graphite, 6 per cent. of carborundum, and 1 per cent. of iron, the rest consisting of other impurities; but the identity of the oxygen compounds present is still a matter of conjecture.

Siloxicon, which is manufactured by the International Acheson Graphite Company, is a greenish-grey, amorphous substance, containing dark particles of graphite and carborundum. It has a specific gravity of 2.52, is extremely refractory towards heat, chemically inert, and is insoluble in molten iron. The temperature of its formation is about 1,600°, while at 1,840° it breaks down into crystalline silicon carbide, silicon, and carbon monoxide.

It is prepared in a furnace similar to a carborundum furnace, but having three or more resistance cores to obtain a more even distribution of temperature throughout the mass of material. Acheson, who patented the process in 1902, used, as raw material, 1 part of powdered coke to 2 parts of sand, together with sawdust to increase the porosity.

Siloxicon is used alone or with binding material for making crucibles, muffles, and fire-bricks, and as a furnace-lining.

It was at one time thought to have a promising future, but it has not been actively commercialised and is not very largely used at present.

Monox.—H. N. Potter (English Patent 26,788, of 22nd December 1905) and F. G. Tone (United States Patent 993,913, of 30th May 1911) patented processes for the production of a substance which was called monox by the former, and was claimed to consist essentially of silicon monoxide, SiO. The processes consisted in heating a mixture of silica and carbon in a closed resistance or arc furnace, withdrawing the carbon monoxide gas and trapping it in air-free collecting chambers. The gas carried with it the monox, which collected as an extremely fine powder, light brown in colour, and having a true density of about 2.24. Monox is, however, so voluminous that, unless compressed, it weighs only 2½ lbs. per cubic foot. It burns in oxygen to form silica, and is slowly oxidised by water. It was thought to be a mixture of SiO, SiO_2, and Si, but its composition has never been definitely settled. On account of its opacity and power of thickening fluids, monox can be used as a pigment in certain oil paints, particularly for protecting ironwork. It is not manufactured at the present day, however, and its interest is theoretical only.

MANUFACTURED GRAPHITE

Graphite, also known as **plumbago** or **black lead,** is a form of carbon which occurs as a mineral in wide distribution throughout the world, generally in compact crystalline masses. Mineral graphite is velvety black or steel grey in colour, is soft, and has a specific gravity which varies in different localities over a range of about 2.25–2.35. It contains from 79.92 per cent. carbon, the chief impurities being ferric oxide, alumina, silica, and lime.

Graphite is found also in the crystalline form in blast furnace slag produced during the process of iron smelting, where it is known as **kish.**

Graphite occurs, just as does amorphous carbon, in several varieties, both crystalline and amorphous. In some cases there is no sharp line of demarcation between graphite and amorphous carbon, so that a satisfactory definition of the former is difficult to give. W. C. Arsem, who exhaustively studied the subject, proposed to define graphite as that allotropic modification of carbon which has the specific gravity of from 2.25–2.26.

Mode of Formation.—Carborundum, as has already been pointed out, decomposes at a temperature which has been estimated by L. E. Saunders to be about 2,240° C. into its constituent elements silicon and carbon, the carbon taking the form of crystalline graphite. E. G. Acheson, observing that the core of his carborundum furnace was surrounded by a layer of graphite, which sometimes retained the form of carborundum crystals, conceived the idea of producing graphite artificially by first forming silicon carbide in the electric furnace and then decomposing it, by raising the temperature, into graphite and silicon, the latter, together with other impurities, being volatilised by the intense heat. This process, which he patented in 1895, forms the basis of the present-day graphite industry. Acheson subsequently observed the fact that coke could be converted into graphite in the presence of very much less silica than would have been required to convert the whole of the carbon into silicon carbide, and he therefore concluded that the action was catalytic. This observation has been confirmed by Borchers and Mögenburg, and Borchers and Weckbecker, who have shown also that other oxides, such as Al_2O_3, Fe_2O_3, B_2O_3, and CaO, are capable of bringing about the change in various degrees, the required temperature being lower the greater the amount of oxide present. More recently W. C. Arsem has shown that amorphous carbon is converted to graphite at temperatures near 3,000°, even when no oxide is present; thus, petroleum coke gives a good quality of graphite without the aid of an oxide. Most forms of carbon tend to pass to graphite at high temperatures, the velocity of the change being widely variant according to the nature of the substance and the conditions.

Graphite is manufactured by the International Acheson Graphite Company at Nigara Falls, U.S.A.

The original patents for the production of electro-graphite expired many years ago and amorphous carbon, in various forms, is now regularly converted into graphite by heating in an electric furnace for several hours at 2,800°–3,000° C.

Two processes are carried out: (1) the manufacture of graphite powder; (2) the graphitising of electrodes and other moulded articles.

For the manufacture of **graphite powder** a resistance furnace (Fig. 4) similar to the carborundum furnace is used, though narrower in section and having a much thinner core. There are twenty-two furnaces, each being about 30 ft. long, with a sectional area of 18 in. by 14 in., and taking about 1,000 H.P. The end walls, which carry the electrodes E, are fixed, while the side walls, which are made of carborundum fire-bricks are movable. A protective layer of carborundum firesand F is placed at the bottom of the furnace, and the charge M is loaded in by overhead electric cranes. The charge varies according to the quality of graphite required. It generally consists of anthracite, in fine grains containing up to about 10 per cent. of ash.

The ash contains the oxides of silicon, iron, and aluminium, so that a sufficient quantity of oxide to produce the catalytic action is distributed throughout the material. For the best quality of graphite, petroleum coke is used, lumps of coke being embedded in coke powder, and from 2–5 per cent. of ferric oxide added. In this case the oxide is soon reduced, and, as the temperature rises, the volatilised metallic iron permeates the whole contents of the furnace and brings about the required change.

The core C, which consists of graphitised coke, having been placed in position and the furnace filled, the charge is covered with a layer of firesand and the current is passed. At the beginning, about 3,000 amperes at 220 volts are used; but the resistance decreases rapidly, and the final current is some 9,000 amperes at 80 volts. The duration of the run is about twenty to twenty-four hours. When the furnace has cooled, the graphite is carefully removed, ground in tube mills, and sifted from coarse particles by means of air separators.

The world's total production of natural graphite in 1938 was nearly 200,000 tons, about one-quarter of this coming from Korea. Other large producing countries were: Austria, 16,600 tons; Germany, 27,700 tons; and Ceylon, 12,000 tons. Complete post-war figures are not available, though there appears to have been a marked reduction in world output, possibly due to the growing importance of the electro-graphitisation industry.

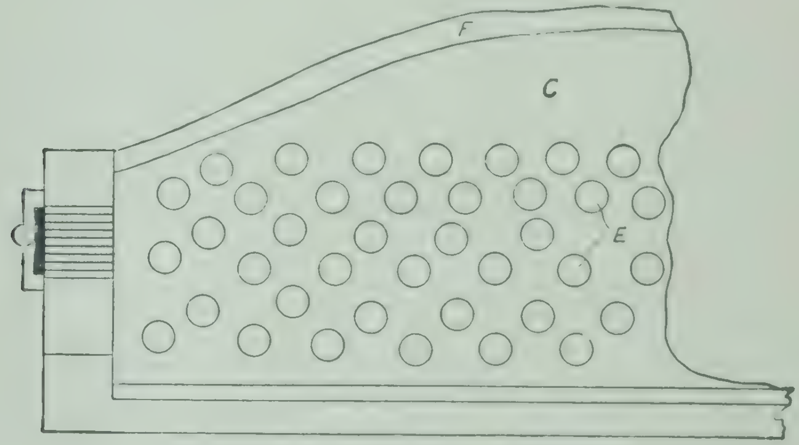


FIG. 4.—Furnace for Graphitising Electrodes.

Manufactured graphite contains besides 1–2 per cent. amorphous carbon, varying quantities of ash, according to the temperature at which it is produced and the nature of the raw material; the quantity of ash may be as high as 10 per cent., but in the purest grades it is about 0.2 per cent.

Uses.—Graphite is used for making electrodes, lamp-carbons, battery fillings, electrical carbon brushes, refractory crucibles and retorts, and for pencils. It is also used as a paint for coating metal-work, and in electrotyping. As a lubricant it is used with or without oil or grease. By treatment with a solution of gallotannic acid, graphite powder can be caused to assume a state of very fine subdivision, so that it remains suspended indefinitely in oil or water.

In this form it is manufactured under the names "Oildag" and "Aquadag," the word "dag" standing for "deflocculated Acheson graphite."

For **the graphitising of electrodes** and other shaped or moulded articles, a furnace (Fig. 4) similar to that described above is used. The electrodes are shaped from a mixture containing 97 per cent. of powdered petroleum coke and 3 per cent. of ferric oxide, a little water and molasses, or tar, being used for binding. The shaping is done either by moulding or by extruding the mixture under hydraulic pressure through a die of the required form. The dried electrodes E are made to take the place of the core of the furnace, being placed in horizontal rows in the furnace, cross-wise to the current stream, and surrounded by granular coke C, by which they are isolated from one another. A mixture of sand and ground coke F covers the furnace. The initial current is 1,400 amperes at 210 volts, while at the end of the run the current is 9,000 amperes at 80 volts. The chief development of heat takes place in the granular coke, so that the surfaces of the electrodes are surrounded by regions of high temperature.

Graphite electrodes contain only about 0.1–0.2 per cent. of amorphous carbon, and about 0.1–0.5 per cent. of ash, the rest of the impurities having been volatilised by the intense heat. The specific resistance is 0.0008 ohm per c.c., or only about a quarter of that of amorphous carbon.

Graphite electrodes are more capable than amorphous carbon electrodes of standing sudden changes of temperature without fracture.

On account of their durability, and the fact that they are comparatively chemically inactive at very high temperatures, graphite electrodes are extensively used in the electro-chemical and electro-metallurgical industries, *e.g.*, in the manufacture of carbides and ferro-alloys, the electrical smelting of iron, zinc, and nickel, the electrolysis of fused chloride and fluoride, the electrolytic recovery of bromine, the production of chlorine and caustic alkalis and of hypochlorites, the cyanide gold and silver processes, etc. They are not used in solutions in which oxygen is liberated at the anode, their temperature of oxidation in air being 640° C.

Shaped graphite blocks, panels and tubes, are also used in chemical engineering applications, particularly in liquid/liquid and liquid/gas heat exchangers, because of the high thermal conductivity of graphite and its resistance to chemical attack.

ALUNDUM

Alundum, or corundum, is fused alumina, Al_2O_3, rendered hard by a special process of melting and cooling. Its specific gravity is from 3.93–4.00, and there are two varieties, one white, of melting point 2,050°–2,100°, and the other reddish-brown, melting at 2,000°–2,050°. The white crystalline variety is 99 per cent. pure, while the brown vitreous product is about 93 per cent. pure. The impurities present consist chiefly of oxides of iron, silicon, and titanium. Alundum has a hardness of over nine on the Mohs scale. Alundum is the trade name of products made by the **Norton Emery Wheel Co.** at Niagara Falls, by fusing pure calcined bauxite in a 500 H.P. arc furnace, and allowing the molten product to cool slowly during three to four hours. The block of alundum so obtained is broken up and used as an abrasive in the form of wheels, etc. It is particularly efficient for work on metals of high tensile strength, such as alloy steels, wrought iron, etc. It is also used for muffles, firebricks, etc.

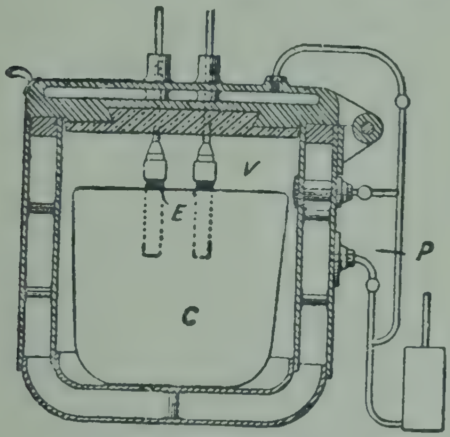


FIG. 5.—Alundum Furnace of Pettigrew and Gerbel-Strover.

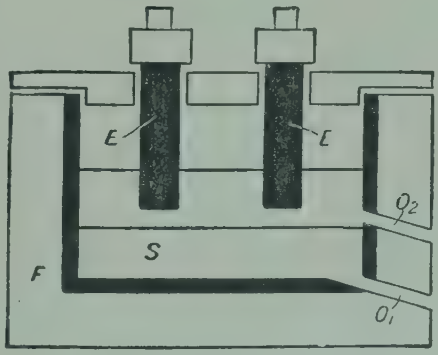


FIG. 6.—Furnace for Producing Silicon.

It is also manufactured at Rheinfelden under the name of "Diamantin."

Fig. 5 shows a design by J. Pettigrew and E. Gerbel-Strover in which the bauxite is fused in the chamber C, which is enclosed by a vacuum jacket V, surrounded by some bad conductor of heat. The electrodes E pass through stuffing boxes in a hinged lid. P represents the arrangement for exhausting the air from the vacuum chamber. The fused material is allowed to cool very slowly in the heat-insulated crucible.

Silicon.—Crystalline silicon is manufactured in the electric furnace by heating together a mixture of silica (quartz or sand), SiO_2, and carbon (coke), when the following change takes place:—

$$SiO_2 + 2C = Si + 2CO.$$

The type of furnace used is an arc furnace taking 1,200 H.P. It is constructed of firebricks F, and is lined with carbon C on the interior (Fig. 6). It carries two depending carbon electrodes E, which extend for a considerable distance into the charge, which consists of a mixture of coke and sand. The silicon S is tapped from the bottom of the furnace, at an outlet O_1, at intervals to form pigs of 600–800 lbs. weight. O_2 is an outlet from which slag can, if necessary, be drawn off. Silicon is manufactured on the Continent in furnaces taking over 1,500 H.P.

Silicon is manufactured by the **Carborundum Company.**

Properties.—Crystalline silicon, as manufactured in the electric furnace, is a brittle substance having a silver-grey lustre and a specific gravity of 2.5–2.6 (cast). It has a hardness of six on the Mohs scale, and is stated by F. J. Tone to melt at 1,430°, though this figure is probably low. It conducts heat and has an electrical resistance many times greater than that of carbon. Acids, with the exception of hydrofluoric acid, scarcely attack it at moderate temperatures; but alkalis readily react upon it. It contains from 90–97 per cent. of silicon, with aluminium, carbon, and iron as the principal impurities.

Silicon is a valuable element for use in metallurgy. It is used in refining steel, in place of the higher grades of ferro-silicon, and also in the manufacture of low carbon ferro-alloys, such as ferro-vanadium and ferro-chromium. In this connection, silicon has the advantage of possessing great heat of oxidation and of giving a solid oxidation product.

A. G. Betts proposed to use silicon as a reducing agent for zinc ores containing impurities such as iron and lead. Recently, silicon castings have been successfully made, and cast silicon pipes, pans, and other articles are turned out. On account of its resistance to the corrosive action of acids, and its advantage over iron in the matter of specific gravity, this silicon ware is of much value in the chemical industries.

FERRO-SILICON

Ferro-silicon is an alloy of silicon and iron in various proportions.

Manufacture.—Ferro-silicon is made by heating together in an electric furnace a mixture of silica (usually quartzite), SiO_2, iron or steel turnings, and carbon (coke, anthracite, or charcoal), when the following changes probably take place:—

$$SiO_2 + 2C + Fe = (Fe.Si) + 2CO.$$

Ferro-silicon.

The raw materials consist of quartzite containing over 95 per cent. of silica; iron or steel turnings or shavings, which should contain very little phosphorus; and anthracite, charcoal, or high-grade coke. Quartzite, anthracite, and coke are used in small lumps, while charcoal is used unbroken. Hæmatite is still employed as a source of iron in certain localities. The proportions of the various materials depend upon their purity and upon the grade of ferro-silicon to be produced. Thus Pick and Conrad cite instances for Rathenau furnaces using anthracite (20.7 per cent. ash, with two thirds silica), quartz (0.5 per cent. iron oxide), and iron turnings: for 25 per cent. ferro-silicon the charge was 40 per cent. quartz, 40 per cent. iron turnings, and 20 per cent. anthracite; while for 52 per cent.

ferro-silicon, the charge was 58 per cent. quartz, 13 per cent. iron, and 29 per cent. anthracite.

Furnaces.—The type of furnace used is very similar in principle to the calcium carbide furnace, and in France furnaces at one time used for carbide manufacture are now employed for ferro-silicon. In all cases an arc is struck between one electrode, or both electrodes, and the charge, so that the action of the furnace is partly an arc and partly a resistance action.

The older (**Rathenau**) type of furnace, some of which are still in use on the Continent, simply consists of a furnace-body, usually cylindrical in section, of fire-brick lined with carbon, into the open top of which a depending, adjustable electrode passes. The other electrode is formed in the hearth of the furnace by means of a steel plate with grooves, into which is pressed a graphite composition. The charge is filled in from the top and reaches to the electrode. The ferro-silicon sinks to the bottom, and is removed every hour or so at a tap hole. The molten substance is allowed to cool, and then broken up into small lumps for transport.

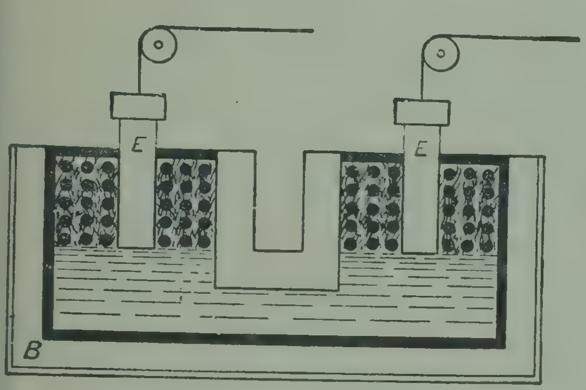


Fig. 7.—Keller Furnace.

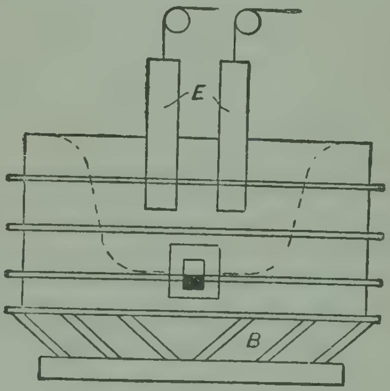


Fig. 8.—Modern Ferro-Silicon Furnace.

This furnace suffers from several disadvantages, in that the electrode consumption is large, and that part of the charge is lost as vapour at the open top.

A more efficient type of furnace is the **Keller furnace,** formerly used by the Keller-Leleux Company at Livet (Isère). This consists (Fig. 7) of a furnace-body B lined with carbon. Two suspended water-cooled electrodes, or groups of electrodes, E, pass through holes in the roof of the furnace; and a tapping outlet enables the ferro-silicon to be drawn off. Slag can also be removed, and the furnace is continuous and may run for several years. The arrangement obviates the disadvantageous floor terminal.

In these older types of furnace the current used is from 10,500–15,000 amperes at from 40–75 volts. At Livet (Isère) some of the furnaces of the Keller-Leleux Company take 1,200 H.P. More modern furnaces are built of silica fire-bricks, bound round with iron frames, and lined internally with carbon. Two adjustable electrodes E (Fig. 8) are suspended by chains so as to pass through shafts in the roof. The furnace is of such a size that the molten material is separated from the walls and iron bottom B by a layer of solidified charge, the solidification of this layer being aided by air-cooling. The tapping is done through a hole in the side of the furnace, the layer of solidified material being pierced by a pointed electrode mounted on a small carriage. The slag can be drawn off as required by piercing at an appropriate height. The electrodes are so adjusted that there is a small clearance between them and the charge, so that an arc plays between each electrode and the fused charge, through a thin layer of vapour in which the action chiefly takes place. By this means the current is prevented from becoming diffused, and a region of very high temperature is available for the reaction. In the production of ferro-silicon an alternating current is generally used; a direct current may be employed, but the product is then less pure, since it contains foreign metals produced by the electrolysis of impurities in the charge. The voltage used varies, according to the circumstances, from about 40–80 volts. Modern furnaces take up to 4,000 H.P., and even larger (5,000–8,000 H.P.) three-phase furnaces are in use in Norway and Austria. The largest furnaces are said to take 10,000 H.P.

Properties.—Ferro-silicon is a hard, greyish substance of crystalline structure, and consists of various compounds of iron and silicon in alloy with either element.

Its composition varies widely, commercial ferro-silicon having a silicon content which may range from about 10 per cent. to over 96 per cent. (see **Silicon**). Silicides of iron having the fomulæ FeSi, $FeSi_2$, Fe_2Si, and Fe_3Si_2, have been definitely isolated, while three other silicides, $FeSi_3$, Fe_3Si, and Fe_3Si_4, are said to exist.

Ferro-silicon, as made in the blast furnace, has a low percentage of silicon, but the modern type of electric furnace has tended to increase the silicon content, the chief grades now made containing about 25 per cent., 50 per cent., 75 per cent., and 90 per cent. of silicon. The 50 per cent. grade is the most used. Different grades of ferro-silicon naturally vary in properties. The melting point may be said to range from about 1,200° to above 1,400°; while the specific gravity, according to J. Rothe, is 6.96 for a silicon content of 11.6 per cent., 6.48 for 24.3 per cent., 4.55 for 47.3 per cent., and 2.93 for 77.3 per cent. Ferro-silicon is a good conductor of electricity, and is magnetic, its magnetic qualities diminishing as the silicon content rises.

Ferro-silicon generally contains as impurities calcium, aluminium, magnesium, manganese, phosphorus (and sometimes traces of arsenic), sulphur, and carbon.

The presence of more than a very small amount of phosphorus is to be avoided, since serious explosions, thought to be due to the generation of phosphoretted hydrogen, have taken place. The grades of ferro-silicon most liable to become explosive are said to be those containing 30–65 per cent. of silicon.

Uses of Ferro-Silicon.—It is used extensively in the steel industry as a reducing agent. For many years one of the great problems of the steel industry was how to diminish or avoid the blow-holes and pipes that were formed when steel was poured from the ladle into the large ingot moulds. It was often necessary to cut off 20–25 per cent. of the upper parts of the ingot before perfectly sound metal was reached. It was found that the addition of quite small amounts, say $\frac{3}{4}$–1 per cent., of ferro-silicon to the steel while in the ladle evolved much heat from the combustion of the silicon. This thinned the metal and absorbed the oxygen dissolved in the steel, with the result that on pouring into the moulds there resulted perfectly solid ingots with no blow-holes at all. This discovery has made ferro-silicon an important article of commerce, and it is being used to an increasing extent in the steel industry.

Ferro-silicon is also used for producing some of the extraordinary acid proof irons now on the market. Ironac, tantiron, duriron, etc., all contain silicon (see Vol. I., **Sulphuric Acid Industry**).

Storage and Transport.—The evolution of poisonous and explosive gases (probably PH_3) from ferro-silicon containing appreciable amounts of phosphorus caused several accidents (see Pellew, "Ferro-Silicon and its Dangers," *Journ. S Chem. Ind.*, 33, 774, 1914). Consequently in July 1912 the British Board of Trade warned shippers that the carriage of ferro-silicon between 30–70 per cent. Si. is highly dangerous, and was prohibited on both cargo and passenger boats. Above and below that grade it can be carried, if broken into pieces and stored for a month before shipment, and packed in strong wooden cases pierced with holes and properly labelled. Ferro-silicon, however, as now made with purer materials, is not dangerous.

CALCIUM CARBIDE

Calcium Carbide, CaC_2, is produced by heating a mixture of lime and carbon in the electric furnace, when the following change takes place:—

$$CaO + 3C = CaC_2 + CO,$$

this reaction being a reversible one. The temperature at which the carbide is produced in the electric furnace is variously given as 3,000°, 2,000°, or lower.

The raw materials consist of freshly-burnt lime, containing little magnesia and alumina; and of anthracite or high-grade coke, containing less than 5 per cent. ash, or charcoal.

The materials are, as far as possible, free from phosphorus, arsenic, and sulphur. It has been found that, as in the case of ferro-silicon, the presence of phosphorus and arsenic gives rise to compounds which may render the acetylene produced from the carbide explosive and highly dangerous. The materials are mixed together and fed into the furnace, by hand, in the form of small lumps.

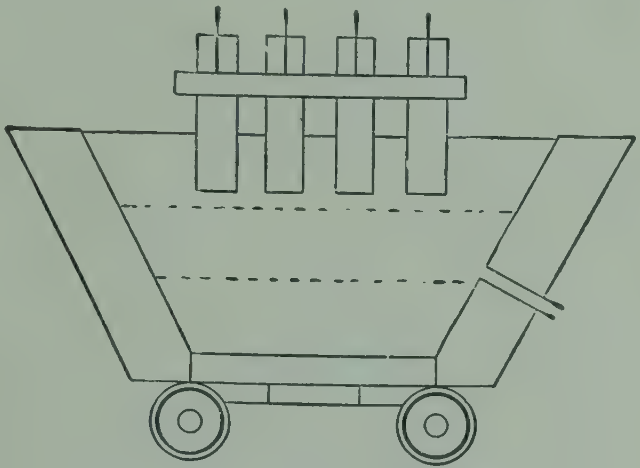


FIG. 9.—The Alby Carbide Furnace.

The electric furnaces used in the various countries in which calcium carbide is manufactured are of many different types. In the majority of the more modern furnaces, in which both electrodes enter the furnace from above, the carbide is tapped in a molten form as described under **Ferro-Silicon**; in others, chiefly belonging to the older types, the carbide is taken from the furnace in solid blocks, the furnace body in which the carbide is formed either being wheeled away or, as in the case of the Horry furnace, being caused to rotate and thus carry the carbide away from the sphere of the electrodes.

In the **modern Alby furnace** (Fig. 9), which is used by the Alby United Carbide Factories at Odda, Norway, the carbide is removed by tapping during the process. It consists of a sheet-iron body lined with carbon and mounted on wheels, one electrode being formed in the hearth by means of a steel grill into which a graphite composition is pressed, while the other electrode is constituted by a group of adjustable carbons depending through the roof. A tapping-hole is provided at one end of the furnace, through which the carbide is withdrawn every forty-five minutes.

Fig. 10 shows a complete carbide plant of 4,000–6,000 kW., as erected in Norway. A is the tapping arrangement which runs on wheels. It consists of a rod about 18 ft. long, at the end of which is an electrode connected to a copper conducting cable K. A powerful current is connected with this electrode, which, when applied to the opening in the side of the furnace closed by the solidified walls of material, melts a hole through $1\frac{1}{2}$ ft. of material in about twenty minutes, so that the white-hot molten carbide flows out and runs off into the iron trays provided for it.

The furnace is built of refractory material lined with carbon. T are the transformers, V the ventilating fans for air-cooling the furnace walls, W the winding gear for raising and lowering the electrodes into the furnace.

The molten carbide is allowed to cool in cast-iron trays, where it forms slabs about 6 in. thick, which are afterwards broken up.

The Odda works formerly contained twelve furnaces, each of about 1,800 H.P. capacity, and one larger furnace; but the number is in process of being more than doubled. The current is stated to be 28,000 amperes at 50 volts, and each furnace is capable of producing 7–8 tons of carbide per day of twenty-four hours. 2,000 lbs. of lime and 1,300 lbs. of anthracite, with less than 3 per cent. of ash, are consumed per ton of carbide. The temperature attained is said to be between 2,800° and 3,000°, and the workmen are shielded from the heat by means of wire screens.

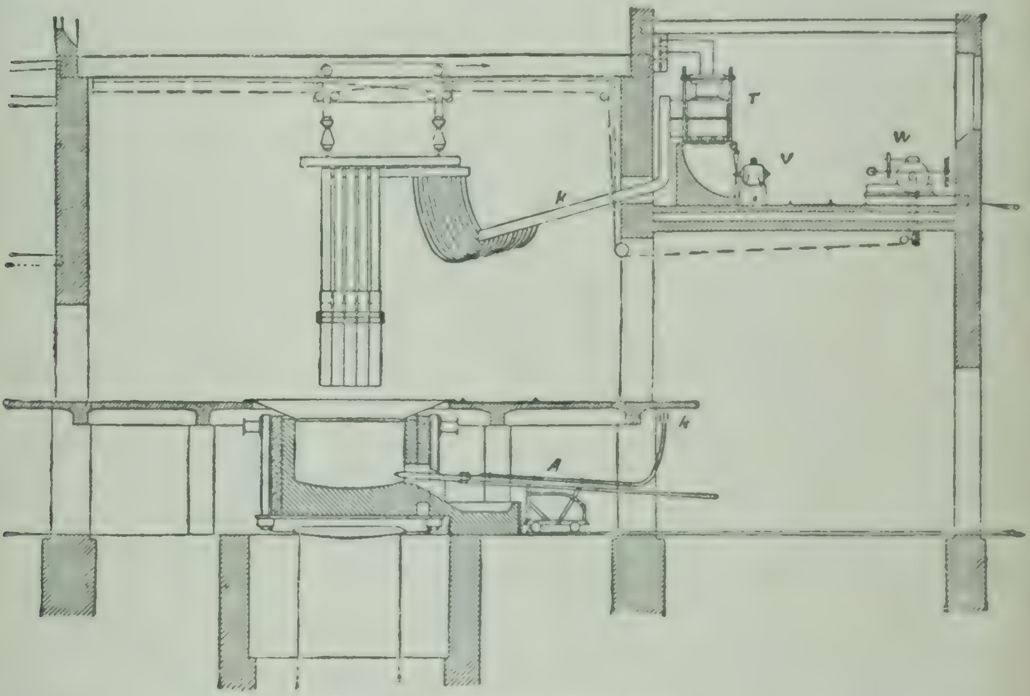


FIG. 10.—Modern Carbide Plant.

At Niagara Falls and at Sault Sainte Marie, the Union Carbide Company employ the Horry type of rotary furnaces.

The furnace consists of a vertical rotating wheel of sheet iron, 8 ft. in diameter and 3 ft. broad. The outer rims are flanged, and over the flanges are placed removable iron segments, 2 ft. deep, so as to form an annular receptacle. These segments are bolted to the lower half of the wheel only, plates being removed as they come by the rotation into the upper half, and placed in position as a space under the electrodes becomes vacant. The electrodes are formed by bundles of carbons, which pass into a fixed vertical shaft, into which the charge is fed. As the carbide is formed, the wheel, which is under automatic electrical control, is caused to rotate, and thus carries the product out of the sphere of the arcs. When the carbide has reached the other side of the wheel, it has had time to cool, and is broken off in pieces 6–9 in. thick. A complete revolution is said to take place once in twenty-four hours. The capacity of the furnace is 500 H.P., and the current is 3,500 amperes at 110 volts.

Both direct and alternating currents can be used for carbide manufacture, though the latter are generally the more advantageous. Recently, very large double, three-phase furnaces have been successfully operated on the Continent. The largest furnaces run up to 10,000 H.P.

Commercial calcium carbide is usually about 80–85 per cent. pure, and always contains lime as an impurity. Carbon and iron are among the other impurities commonly found.

Properties and Uses.—Calcium carbide, CaC_2, in the pure state is a colourless, transparent crystalline substance, but the commercial product is usually greyish or brownish, the colour being due to impurities. It has a specific gravity of 2.22, and is insoluble in all known solvents. At a temperature above 1,500° it decomposes, probably into carbon and a sub-carbide. Its chief chemical reactions upon which its commercial value is based are, firstly, its property of reacting with water in the cold to give **acetylene gas** (see **Martin's** "Industrial Chemistry: Organic"), which is used to a very large extent for welding and synthesis:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2;$$

and secondly, the power of combining with nitrogen at a temperature of about 1,200° to form **calcium cyanamide** (see Vol. I.), which is used as a fertiliser under the name of "**nitrolim**," or is employed as a basis for the production of ammonium sulphate (see Vol. I.):—

$$CaC_2 + N_2 = CaCN_2 + C;$$
$$CaCN_2 + 2H_2O + 2H_2SO_4 = (NH_4)_2SO_4 + CaSO_4 + CO_2.$$

Calcium carbide was first prepared by Wöhler in 1863, by the action of a molten alloy of zinc and calcium on carbon; he obtained a black substance which evolved gas on treatment with cold water. In 1892 both Willson and Moissan independently rediscovered the substance, and the first-named placed the process on a commercial basis. The first commercial production of calcium carbide was made by the Willson Aluminium Work in America in 1892, and since that time the industry has extended to enormous dimensions.

The largest carbide plants are situated at Niagara Falls (U.S.A.); Sebenico (Austria); Odda (Norway); Sault Sainte Marie (U.S.A.); Ascoli (Italy); Viège (Switzerland); Collestate (Italy); Papigno (Italy); Jajce (Bosnia); Méran (Austria); and Notre Dame de Briancon (France).

Boron carbide, B_4C, is an exceedingly hard, inert substance, made by heating together boric oxide with coke in an electric furnace. It is used for making blast nozzles, drawing dies, thread guides, and as an abrasive (see page 433).

Modern Electrothermal Processes

An excellent review of electrothermal processes for the reduction of ores was given in the recent Castner Memorial Lecture by C. H. Aall.(1) In this review the development of electric smelting furnaces has been considered in detail, with particular reference to the development of large furnaces using three-phase current and Söderberg electrodes. Such electrodes, described below under the heading "Production of Pig-iron", are now in general use for the manufacture of carbide, pig-iron, ferro alloys, and aluminium. The Söderberg electrode is continuous in operation, it is simple and cheap to operate, and it is available in larger sizes than prebaked electrodes. It is, however, unsuitable for the manufacture of phosphorus because the low electrode consumption in this process does not justify the higher installation cost of the continuous electrode.

Reduction of Phosphorus.—Perhaps the most rapid expansion of the use of the electric furnace for reduction purposes in recent times has been for the preparation of yellow phosphorus. This expansion has reached greatest proportions in the

U.S.A., where production has more than doubled during the last ten years. Production during 1949 in the U.S.A. was 250,000,000 lbs.

Production of Pig-iron.—The use of the electric arc furnace for the reduction of iron ores has also been developed considerably in recent years, particularly in countries such as Switzerland, Italy, Hungary, India, Japan, and Scandinavia, where electrical power is cheap and coking coal is not available. The commercial application of this process became a practical proposition with the development of the Tysland-Hole furnace in Norway during 1928. The development during the last war in Switzerland is typical of the use of the electric furnace for such purposes and it will be useful to describe this in some detail.

Shortly before the war, a commission was established in Switzerland to study the reduction of iron ore in the electric arc furnace using the poor quality anthracite available at Valais as the reducing agent. The processes examined were those previously investigated in Norway and Sweden, particularly that of Tysland-Hole. An experimental unit was set up at Wimmis with a furnace of capacity 3,000 kilowatts, and with three electrodes in line, in order to study the reduction of the various ores available in Switzerland by the native anthracite.

The results proved conclusively that this was a practical technical process and a similar unit was erected and operated during the period 1939 to 1944 at Flums, producing some 25,000 tons of iron from the ores found at Gonzen with an average iron content of 50 per cent.

This quantity is very small compared with the pre-war Swiss requirements of iron, averaging 60,000 tons per annum, and in 1941 the Society of Factories of Louis de Roll decided to erect a unit for the production of 50 tons of pig iron per day based upon the Tysland-Hole process, to replace the blast furnace at their Choindez works.

The electric furnace at Choindez contains three electrodes of the Söderberg type, arranged at the corners of an equilatoral triangle and dipping into a totally enclosed, vertical, cylindrical, refractory and carbon lined furnace, of dimensions approximately four metres high by six metres diameter. The refractory furnace is enclosed by a steel shell, the lower portion of which is water cooled. The whole furnace rests on a massive brick foundation, and sand lined runways lead to the casting bay, where the pigs of iron are made, and to the pit, where the slag is quenched with water.

A mixture of lime, iron ore, or waste products containing iron ore or iron, with coal or coke in suitable proportions, is fed continuously to the furnace by means of chutes arranged on its outer periphery. The gas produced is taken off from two gas outlets, fitted at opposite sides of the furnace, a slight positive gas pressure being maintained inside the furnace. The gas produced is passed through Theisen washers to remove entrained dust and is used for melting the charges in the foundry and for other purposes.

Electric current is received at 45,000 volts and is transformed down to between 80 and 150 volts in a 7,500 kVA transformer. The electrodes consist of light welded sheet steel shells partly filled with Söderberg paste, and supported and fed to the furnace by means of hydraulic equipment. The Söderberg paste consists of a mixture of anthracite, coke, resin, and tar, and this is added from time to time so as to maintain a level of 2–3 metres in the electrode shells. As the shells move downwards into the furnace, where they are gradually consumed, new shells are welded on at the top.

Raw Materials.—The raw materials used are all of Swiss origin, the exact composition varying according to the availability of the various minerals and waste products. Amongst the ores used are limonite from Delemont, containing [illegible] per cent iron, 15 per cent. SiO_2, and 13 per cent. Al_2O_3; magnetite from Montchemin, containing 45 per cent. Fe, 17 per cent. SiO_2, 8 per cent. Al_2O_3, 5 per cent. CaO, 6 per cent. MgO, and haematite from Gonzen, containing 48 per cent. Fe, 5 per cent. SiO_2, 10 per cent. CaO. Also residues from the oxidation of pyrites for the manufacture of sulphuric acid, agglomerated with 10 per cent. powdered coke, may be used after a preliminary heating process to cause the agglomerate to sinter together.

Calcium carbonate of excellent quality, containing 53 per cent. of calcium oxide, is available from the hills surrounding the factory at Choindez.

The anthracite used as the principal reducing agent is very inferior as a fuel, and contains up to 50 per cent. ash. A small amount of coke from a nearby gas works is also used on occasions.

The amount of carbon added is sufficient to combine with the oxygen in the iron ore to produce carbon monoxide, with about 10 per cent. added in excess of this quantity. The amount of lime added is sufficient to cause the impurities to form a readily fusible slag at the operating temperature of 1,380°–1,410° C.

A formula is established for each type of raw material and the quantities are weighed out in small batches and transferred batch by batch to the individual hoppers feeding the chutes leading to the furnace. No other mixing is necessary. The materials are usually not ground, but are used, as received, in all sizes from lumps 3 or 4 inches in diameter down to dust, though on occasions some attempt has been made to remove some of the dust so as to reduce the load on the gas washing plant. The material flows down the chutes by gravity, without requiring poking or other attention.

The electric arc furnace supplies most of the heat required and, for normal mixes, the amount of electrical energy is between 2,500 and 3,000 kW per ton of pig iron produced.

Products of the Process.—The Swiss iron ores contain little phosphorus and most of the sulphur present in the raw materials appears in the gaseous products. A typical analysis of the pig iron produced is:—

Carbon	3.6–4.2	per cent.
Silica	1 –3	,,
Manganese	.2–1.0	,,
Phosphorus	.2– .3	,,
Sulphur	.05 (max.)	

The quantity of carbon necessary for the reduction is from 3–400 kg. per ton of iron.

The slag and iron are tapped off every four hours in batches of approximately 8 tons. The consumption of the electrodes is about 15–16 kg. per ton of iron.

The production of slag is usually 75 per cent. of the weight of the iron and its composition depends upon the amount of lime added to neutralise the acidic constituents. Its composition normally varies within the following limits:—

CaO	40–45	per cent.
MgO	1–10	,,
Silica	25–30	,,
Al_2O_3	15–25	,,

The composition of the slag can be adjusted so as to be within the limits required of a good Portland cement clinker, and at Choindez the powdered product obtained from quenching the slag in water is sold to a local cement works for mixing with cement clinker as normally produced. It can, of course, if desired, be used for the preparation of slag wool or any of the foamed slag products. The pig iron produced is suitable for use in foundry work, and at Choindez the whole of the production is used in the local foundry and for spun cast iron pipes, mixed with whatever quantity of scrap material is available.

Production of Gas.—The gas is of fairly high calorific value and is highly toxic, containing about 70 per cent. of carbon monoxide, 16 per cent. of carbon dioxide, 10 per cent. hydrogen, and small quantities of methane and nitrogen. Its calorific value is about 2,500 calories per cu. metre (275 B.Th.U.'s per cu. ft.) and the quantity produced is from 1,200–1,400 cu. metres per hour. During the day-time all this gas can be used effectively in the foundry, but at night it is usually burned to waste.

General Experience of Operation.—The plant at Choindez has operated intermittently without any serious trouble since 1943, and, when running, has produced an average of more than 50 tons of high quality pig iron per day. It has been closed down on several occasions during winter when electricity has not been available, but on each occasion it has not been necessary to empty the furnace, and the unit started up after each shut-down without any trouble. On one occasion the unit ran for fourteen months continuously, without shutting down for any reason, and with no mechanical trouble. The original carbon and refractory linings are still present and they have not been patched or repaired in any way.

Technical Advantages of the Process.—The following technical advantages are associated with the electric arc process for the reduction of iron ores as compared with the conventional process of reduction by metallurgical coke in a blast furnace:—

1. Any type of iron ore containing greater proportions of iron than about 25 per cent. can be processed satisfactorily.
2. Waste ferruginous products, such as those from the combustion of pyrites, can be reduced satisfactorily.
3. Any type or quality of carbon or coal can be used without any special preparation or cleaning process.
4. The coke making process is completely eliminated.
5. All the by-products of the reduction can be utilised satisfactorily, including
    - (*a*) the slag as cement clinker or for insulating compositions, and
    - (*b*) the gas for heating purposes.
6. The plant can be started up or shut down at will without taking any special precautions.
7. The plant is cool and clean in operation and is easy to control.

Cost of Process.—The capital cost of the complete plant was about 3,000,000 Swiss francs, which is considered to be very much lower than the total cost of a blast furnace and coke producing plant of equal capacity.

With electricity costing 2 centimes per kW, which is the normal summer charge for electricity at Choindez, it is said that the cost of production of pig iron is about 250 Swiss francs per ton. These figures are equivalent to a charge for electricity of .28d. per kW and a cost of production of pig iron of £14, 10s. 0d. per ton.

It will be seen that the commercial possibilities of the process depend very largely upon the cost of electricity. Under normal circumstances, using 3,000 kW per ton of pig iron, and with electricity at .28d. per unit, the charge for electricity will be £3, 10s. 0d. per ton. Only about 900 lbs. of coal will be used per ton of pig iron as against 18 cwts. of coke in blast furnace practice, and inferior grades of coal can be used, whereas in normal practice only the best grades of coking coals can be used, and those only after converting into good metallurgical coke. A credit item for the electrical process is the good quality of the cement clinker that can be made as a by-product. Consequently, a very strong case can be made out for the use of this process in all countries where electricity is cheap and where a high quality coking coal is not available.

The plant at Choindez was designed and installed by the operating firm, Société Louis de Roll, in conjunction with the firm of Brown Boveri, of Baden. The editor is indebted to the management for the information given above.

Reduction of Aluminium and Chrome.—The reduction of aluminium and chrome ores is also possible using the Tysland-Hole processes, but these reduction processes are not quite so simple to operate as in the case of iron. In the case of aluminium it is very necessary for the coal used to contain extremely small proportions of ash and, particularly, small proportions of silica and sulphur. The ash content of the coal used should not be greater than 1 per cent. and the proportions of silica and sulphur should be less than .3 per cent. of the coal used. A somewhat higher consumption of coal is used in the case of aluminium, the usual quantity used being 15 cwts. per ton of aluminium produced. In the case of chromium, the operating temperature is much higher, and the nature of the coal or coke used in the furnace proper is a determining factor in the success or failure of the operation. Normally speaking, metallurgical coke of a high reactivity and low ash content must be used, but coking coals of volatile matter content of between 22 per cent. and 28 per cent. are also satisfactory.

Powder Metallurgy.—The technique of powder metallurgy enables powders to be formed into solid products by heating at temperatures below their melting point during, or subsequent to, the application of pressure. This technique is particularly valuable in forming wire or moulded products from refractory elements, such as tungsten carbide. It may also be applied to the preparation of solid products from less refractory metals, such as copper, silver, or gold, where the process of powder metallurgy offers any advantage over conventional techniques. The process consists of pressing together, in a suitable mould, at pressures up to 30 tons per sq. in., suitably sized particles of the element or mixture to be formed. A solid block of the material is formed in the cold, but this is weak and must be handled carefully. The moulded product is then raised gradually to a temperature as near to the fusion point as possible, though temperatures between one-half and three-quarters the melting point of the product are sufficient for most purposes. During this process, which is known as sintering, metal to metal bonds develop within the atomic structure, so that the final product is the solid form of the metal or compound. Alternatively, pressure may be applied during the heating process, which is preferably carried out in an electric furnace within the platens of a hydraulic press.

The earliest solid metals manufactured in this way were platinum and tungsten, but the technique has greatly developed in recent years, particularly in the direction of producing mixed products of value in the engineering trades, such as the introduction of graphite into bronze for self-lubricating bearings, for the manufacture of copper and copper-carbon brushes for electrical motors and for the formation of diamond caps and abrasive wheels by sintering industrial diamond powder into metals, such as iron.

Moulded carbon products may also be made in this way, and products such as tungsten carbide or non-ferrous alloys such as stellite. For the manufacture of tungsten carbide, the tungsten and carbon powders are mixed intimately, moulded into shape, and then sintered at about 1,500° C. Stellite is made from a mixture of about 60 per cent. cobalt, 30 per cent. chromium, and 10 per cent. tungsten Tungsten carbide and stellite are extremely hard and are extensively used in engineering and mining as tool tips for cutting or drilling extremely hard alloy steels, cast iron, glass, or rocks. The attainment of the maximum degree of hardness is associated with brittleness, so the normal range of cutting tools or tips with tungsten carbide as base also contain cobalt, or titanium carbide, in varying proportions. The various grades of Wimet, tungsten carbide, are products of this type. For metal turning, Wimet is prepared in the form of tips which are brazed to shanks, generally made of 0.5 per cent. carbon steel. These tools retain their hardness up to red heat, they are self-tempering and capable of cutting at many times the rate of ordinary tool steels. Corresponding products of German manufacture are the Widia products manufactured by Krupps and described in the B.I.O.S. and F.I.A.T. publications quoted in the literature.

REFERENCES

(1) C. H. Aall, *Chem. and Ind.*, **52**, December 30, 1950.
(2) "La Reduction du Mineral de Fer au Four Electrique en Suisse." *Jour. du Four Elect* Oct.–Nov. 1946 et Dec. 1946–Jan. 1947.
(3) "Kritische Studie der Verfahren zur Gewinnung von Eisen aus Eisenerzen unter Verwendung elektrischer Energie." *Sonder. a. d. Schw. Tech. Zeit.*, Jahrgang 46, No. 5, Verlag Art. Institut Orell Fussli A.–G., Zurich.

SECTION LXXXVII

GRINDING AND POLISHING MATERIALS

By Alfred B. Searle
Consultant on Abrasives

LITERATURE

There is very little literature of a special character on grinding and polishing, and the reader would do well to study the chapters dealing with these subjects in works dealing with the particular trade in which he is interested—metal working, lens making, etc.

The following books deal specially with the use of grinding wheels:—

A. B. Searle.—"Abrasives." London, 1935.
A. Haenig.—"Emery and its Industry." London, 1912
G. T. Stier.—"Die Heutige Metall-Technik." 2 Band. (Schleifmittel und Polieren.) Leipzig, 1911.
F.I.A.T. 370.—"The German Abrasives Industry." 1945.

Articles on this subject are occasionally published in the Engineering Journals, and the makers of the various appliances also issue descriptive pamphlets.

Note. In this section, the term **grinding** is restricted to the removal of projections from an uneven surface. For information on crushing or grinding large lumps to powder see the Index.

Materials for grinding and polishing are necessarily of an abrasive character, as their action depends on the removal of projections on the surface to be ground or polished. The two processes of grinding and polishing are closely allied to each other, polishing usually being the final stages of grinding, though sometimes accompanied by a filling up of hollows which is not really a process strictly to be included under grinding. In order to act effectively, grinding materials must have a hardness greater than that of the material to be ground, and the same is largely true of polishing agents; but whereas in grinding, an agent of much greater hardness than the one to be ground will usually prove economical, because of the speed at which it can be made to operate, the use of too hard a material in polishing will prevent a satisfactory polished surface being obtained as it will cut too much into the surface to be polished. It is, therefore, necessary in polishing to use a series of abrasives, the earlier members being hard and rapid in action, and the later ones progressively softer so as to exercise a regularly diminishing action. To some extent, this effect may also be produced by reducing the size of the grains of the abrasive; thus, a very rough piece of steel may be first trimmed with a fine chisel, which will remove any prominent projections. It may then be turned in a lathe, which will produce a still smoother surface; the polishing may be continued by the use of coarse emery powder, followed by emery powder of greater fineness, and the final polish may be given by the use of rouge or lime.

Many polishing materials are softer than the surfaces to be polished, but the pressure at which they are applied gives them the effect of a greater hardness. Thus a series of cloth discs, mounted so as to form a sort of wheel, is composed of an extremely soft material, but by revolving the cloths at a high rate of speed they appear to become quite hard, and form a very efficient polishing tool, particularly if fed with rouge or lime.

Some polishes do not require to be hard enough to abrade the surface to be polished, but only sufficiently so to remove tarnish; this is particularly the case with polishes for gold, silver, furniture, etc.

Grinding materials and polishes may be divided into a number of groups, but a satisfactory classification is not possible. The most important are:—

(*a*) **Hard mineral abrasives,** such as diamond powder, steel, carborundum, emery, corundum, boron carbide, and sand.

(*b*) **Mild mineral abrasives,** such as chalk, rouge, pumice, kieselguhr and tripoli powder.

(*c*) **Waxy polishes,** used chiefly for wood leather, boots, and shoes, etc.

The abrasive particles may be in massive form as in millstones, grinding wheels, rubbing blocks, etc.; some of these are natural stones cut to a suitable shape, whilst others, *e.g.*, emery wheels, are made by mixing an abrasive powder with a suitable binding agent or **bond.**

ABRASIVE STONES AND WHEELS

Mill-stones, such as are used in flour mills, operate horizontally, the material being crushed or ground between the upper and the nether stone. The stones are made of selected rock, chert being preferred, but sandstone being also used extensively. In the grinding of raw materials for the potteries, a mill consisting of a stone pavement over which is dragged a circular frame containing large lumps of chert or other hard stone is used, the material being crushed between the two.

The **grindstones used for sharpening** edge-tools are carved from stones selected from the millstone grit deposits, particularly those in Derbyshire. They wear rapidly, require frequent dressing, and produce a large volume of dust of an injurious character. Since their replacement by grinding wheels made artificially (as described below) "grinder's phthisis" has been almost exterminated. A corundum wheel will last about twenty-five times as long as a gritstone wheel, so that the risk of the dust from it injuring the lungs of the user is negligible.

Abrasive grinding wheels are made of **abrasive** material formed into a disc of convenient size and rotated at a peripheral speed approaching 6,000 ft. per minute. Such grinding wheels have proved invaluable in the dressing of castings and for a variety of other purposes, and in some large works they are rapidly replacing lathes on account of the greater speed at which they work. For many purposes, such grinding wheels can be operated in a stream of water, and the metal to be dressed is therefore kept quite cool, and its temper is retained without much difficulty.

Grinding wheels are of many different types and are made in a great variety of shapes, sizes, and hardness, so as specially to be suited to the requirements of the users. One large firm in the United States claims to have over three hundred different types of wheel in stock, and makes wheels with some thirty-six different degrees of hardness.

Abrasive wheels consist of two ingredients: (i) the abrasive, and (ii) the bond which holds the abrasive grains together.

The **abrasive** may be composed of emery, carborundum, corundum, alundum, or other suitable material, and the **bond** may be (*a*) vegetable, as shellac, rubber, or "boiled" linseed oil and resin, (*b*) siliceous, as water glass, (*c*) vitrified, as in porcelain or ceramic wheels, (*d*) cementitious, as in wheels bonded with cement, (*e*) synthetic or plastic, *i.e.*, composed of one of the modern synthetic resins.

Wheels in which fragments of diamonds are embedded in a suitable bond are particularly suitable for dressing tools with tungsten carbide tips and glass articles.

The wheels made with a vegetable bond are elastic, but their speed of cutting is limited by the temperature at which the bond "burns," and is therefore somewhat low. Wheels with a siliceous bond can be worked more rapidly, but the most rapid wheels of all are those with a vitrified bond. It has been found that wheels having a bond of Portland cement are unsatisfactory, as the cement occupies the spaces between the grains of abrasive in such a manner that instead of allowing a clean cutting abrasive action, the wheel becomes polished or "glazed,"[1] and then fails to cut properly, as its cutting fragments have been covered with cement. Wheels made with sorel cement (magnesia and magnesium chloride, see pp. 137–139) are also unsatisfactory, as they are readily decomposed by water.

In vitrified wheels, the bond is usually a mixture of finely ground felspar and a vitrifiable clay with or without flint or other form of free silica. The bond, when heated, must be highly viscous or it will not grip the particles sufficiently firmly.

The **ideal abrasive wheel** would be one in which the particles of abrasive are held together by the bond until they are worn away or until they become too dull to cut, after which the bond surrounding such particles would break off, leaving a fresh surface to continue the grinding. Hence the bond must be of such a nature and in such a proportion that it is reduced to powder at the same rate as the abrasive particles are worn away; otherwise the wheel will have to be "dressed" frequently. This is objectionable for various reasons, though an occasional dressing is almost unavoidable.

The wheels are manufactured by mixing the abrasive and bond in suitable proportions so as to form a plastic paste, which is filled into a mould made of either wood or steel according to the number of wheels required. In some cases the moulded mass is compressed hydraulically in order to give it added compactness and strength. According to the nature of the bond, the moulded mass must be left to "set" or heated in some way whereby its bonding properties may be fully developed. Wheels with an elastic or siliceous bond are baked at a temperature of 150°–200° C. Those with a vitrified bond require to be heated for sixty hours in a kiln, the final temperature attained being about 1,400° C. The rough wheels have a shaft fitted to the central hub, and are turned true by means of diamonds or "dressing tools" of exceptionally hard steel, after which they are ready for use.

The manufacture requires considerable knowledge of a special character and a high degree of technical and mechanical skill, for very severe conditions are involved in use and the tests applied to the finished wheels are necessarily far more severe than those applied to most other materials, for first-class grinding wheels must stand an enormous peripheral speed of rotation and be capable of being brought up "dead" against the material to be ground without there being the slightest likelihood of the wheel flying to pieces or being crushed in the impact. In order to drive such a wheel at its highest speed it is necessary to see that it is perfectly balanced; this is one of the chief objects of turning or "dressing it" before offering it for sale.

The two chief characteristics of abrasive wheels are the fineness of the texture (due to the size of the particles of abrasive and known as the **grain** or **grit** of the wheel) and the hardness[2] or resistance to crumbling (technically known as the **grade**). The various grades are produced by altering the nature and proportion of the bond used to hold the grains together.

The fineness or sizes of grain in the abrasive are usually expressed by a series of numbers,[3] and the hardness or grade is represented by a series of letters, arranged alphabetically, A representing the softest and Z the hardest grades. The following table by Burley shows the classes of work for which the various grades are most suitable; it is, however, very incomplete, as no indication is given of the nature of the abrasive nor of the bond used.[1]

---

[1] "Glazing" is one of the commonest defects of grinding wheels. It is usually due to (*a*) a wheel with too hard a bond, (*b*) a wheel which rotates too rapidly, (*c*) too much surface in contact with the work, (*d*) insufficient pressure on the wheel or surface to be ground, and (*e*) an excessively abrasive bond which "smears" the abrasive particles instead of falling away.

[2] When manufacturers speak of hard or soft wheels they refer to the behaviour of the wheel as a whole, and not to the abrasive or bond of which it is composed.

[3] Nominally the number of holes per running inch in a sieve which will just pass the particles.

TABLE GIVING GRADE AND GRAIN FOR DIFFERENT CLASSES OF WORK.

Class of Work.	Size of Grains.	Degree of Hardness.
General machine work	30—36	N—P
Tool grinding	20—30	N—Q
Malleable-iron castings	16—20	O—R
Chilled-iron castings	16	P—R
Wrought iron	16	O—Q
Car-wheel grinding	20	N—R
Drop forgings	30	P
Twist drills	46	K—N
Reamers and taps	46—60	K—N
Milling cutters	46—64	K—N
Steel castings	16	P—R
Brass castings	30	M—Q
Bronze castings	20	O—P
Lathe and planer tools	20—36	O—Q
Small tools	60	N—P
Woodworking tools	46	K—N
Rough grinding	16	O—Q
Surface work on steel	20	M—P

H. Darbyshire has published the following figures showing the fineness of wheels specially suitable for the materials mentioned:—

Marble	2 to 6
Glass	16
Soft cast iron	24
Hard cast iron	46
Bronze	60 to 80
Machine steel or cast steel (either hard or soft) where rapid reduction of stock is required, and up to 60 grit when high finish is desired	24

For precision work in engineering shops, wheels containing several sizes of grains are used. Thus, for most purposes, a wheel made of 24, 36, 60, and 80 grit has all the advantages of a 24-grit one, together with the finishing power of an 80-grit wheel and greater economy in use.

Diamond Wheels in which fragments of diamonds are embedded in a suitable bond are particularly used for very accurate grinding and the fine polishing of hard materials. They are more expensive and work more slowly than the more usual abrasive wheels so that the latter should be used for preliminary grinding or smoothing and, where necessary, the final work may be done with a diamond wheel. Diamond wheels are particularly suitable for dressing tools tipped with tungsten carbide and for grinding glass lenses.

Diamond wheels are only "surfaced" with the diamond-bond mixture, the bulk of the wheel being made of steel so as to reduce the amount of diamond to the minimum. The diamonds are embedded in a plastic (resinoid) bond or in metal.

The most important characteristics of such wheels are: (i) the size of the diamond fragments (*grit*), (ii) the ratio of diamond and bond, and (iii) the depth of impregnation.

There are four sizes of grit, viz., 130, 200, 300, and 400 mesh. The sizing should be accurate with a complete absence of fines.

---

[1] Most manufacturers of abrasive wheels, etc., will advise as to the most suitable bonds, grades and grits for the purposes for which their goods are used.

The ratio of diamond to bond affects the rate of removal of metal from the surface being ground.

The depth of impregnation of the mass with diamonds determines the "life" of the wheel.

The best peripheral speed is 6,000 ft. per min.; speeds less than 5,000 ft. per min. result in a low rate of grinding and excessive wheel wear. Light feeds and low pressure ensure the best results.

Diamond wheels should seldom be used dry[1]; a coolant is usually necessary to prevent over-heating of the wheel. All the ordinary coolants are suitable for use with diamond wheels.

HARD ABRASIVE POWDERS

The hard mineral abrasives, either in the form of wheels, as just described, or in powdered form, are extensively used for grinding and polishing. They are sometimes used for cutting, as in the cutting of stone blocks by a band of steel with wet sand as the real cutting agent, but their chief use is for grinding and polishing. The most important of the harder abrasive powders are the following:—

Diamonds in the form of either fragments or coarse powder form the hardest abrasive material known. It is used by lapidaries in the cutting of gems and precious stones, and for other work in which no softer abrasive can be used economically. The larger fragments of diamond are held in a special clamp and are employed as cutting tools, but the smaller fragments are used as powder, applied to the surface to be ground under pressure, water being also used to prevent loss by the flying dust.

Silicon Carbide, SiC, is prepared by fusing a mixture of petroleum residue, coal, or pitch, with fine quartz sand and a little salt in an electric furnace. It has a hardness closely approaching that of diamonds, and is extensively used in the manufacture of grinding wheels and artificial grinding stones.

On account of its hardness it is rapidly replacing corundum in some industries, though it is more brittle.

The crystals of this carbide are small with sharp edges which are just brittle enough to break slightly in use and thus produce a material which cuts cleanly and rapidly and prevents glazing, so that carborundum forms one of the best of the hard abrasives.

Carborundum and Crystolon are trade names for silicon carbide manufactured by two firms respectively.

Corundum, Al_2O_3, occurs naturally and, in an impure form, as **emery**; it is prepared artificially on a large scale in the neighbourhood of the Niagara Falls, U.S.A., by fusing bauxite or other forms of alumina in an electric furnace, and it is (when made by one firm) known as **alundum**. Another variety—a by-product of the thermite welding process—is known as **corubin.**

Emery is found chiefly in the Greek island of Naxos, and consists of an aggregate of crystalline alumina (corundum) and magnetite (iron oxide), with about 12 per cent. of other minerals, of which the chief is tourmaline. The best qualities contain about 50 per cent. of corundum. Deposits of lesser importance also occur in the states of New York and of Massachusetts, whilst a deposit of very pure corundum occurs at Hastings County in Canada.[2] The grinding power of emery depends almost entirely on the proportion of corundum it contains, and on the effect of the other ingredients in detracting from the hardness of this material; it is therefore probable that with increased facilities in the manufacture of artificial corundum of a purity far greater than that of emery, the artificial material will effect a severe competition with the naturally occurring emery, especially where precision grinding is concerned. At the present time, however, the cost of the artificial corundum is so high that there is ample scope for the continued use of emery for some time to come, particularly as the natural material has been found to be more reliable than some of the artificial product.

---

[1] This is particularly the case with metal-bonded diamonds.

[2] The Canadian deposit supplies the best **natural** corundum on the market.

Electrite and Carbo-corundum clay are compositions—the nature of which is kept secret—intermediate between artificial corundum and emery in hardness.

Corundum, emery, and similar materials must be ground before they can be used; the ground product is sifted into thirty-three sizes of grains.

The coarser grains are known by the number of holes per linear inch in the sieves through which they have last passed, but grains finer than those which are retained on a 250 sieve are separated by levigation, and are marked according to the number of minutes they remain suspended in water. No numbers are used for this purpose, but the fineness is indicated by the number of cyphers, thus 0 is the coarsest and 00000 the finest levigated emery.

Emery, corundum, and several other abrasives are mounted on cloth or paper and sold under the names of **emery cloth, emery paper, sand paper,** etc., (p. 439).

It is customary to employ **garnets** on paper used for wood-working, carborundum or emery cloth for leather goods, and corundum, carborundum or emery cloth for general machine work.

Sand (impure silica) is largely used for abrasive purposes, both in its natural form and as sandstone. The grinding stones used for flour mills, cutlery, and other purposes were formerly made of selected sandstone, but synthetic wheels of silicon carbide or corundum are now generally used.

For polishing, sand and water make an excellent abrasive for metals, glass, and other relatively hard surfaces. In the form of a miniature sand storm, sand has been used with great success for grinding and smoothing complex surfaces, and the sand-blast is now considered essential in several industries. In glass manufactories, sand is used in the production of ground glass and for polishing lenses, and in the metal industries it is employed for cleaning and finishing castings, the sand grinding off the dirt and aggregations due to casting in a simple and rapid manner. Sand is not nearly so hard as corundum, but its low cost is greatly in its favour, and it is sufficiently hard for many purposes, so that there is little or no advantage to be gained, in such cases, by using the more costly material unless very rapid work is to be done, or the articles to be ground must be "cut" with great accuracy, as in precision grinding.

Crushed steel, made by heating steel to bright redness and quenching it suddenly in water, is a popular abrasive in the United States, especially for stone and marble dressing, about 600 tons per annum being used for this purpose.

The hardest of all artificial abrasives is the recently discovered boron carbide B_4C, known as "**norbide**." This is made by fusing together boric oxide and coke and has a hardness on Mohs' scale greater than 9.

MILD MINERAL ABRASIVES

The mild mineral abrasives are almost invariably used in the form of powders, and are employed more for polishing than for actual grinding, though, as already explained, the two processes are almost identical.

Chalk, $CaCO_3$—preferably in the form of precipitated calcium carbonate, which is more free from grit than ground natural chalk—is an extremely mild abrasive, much used in the manufacture of dentifrices, and of polishing powders for silver and plated goods.

Hydrated Lime, $Ca(OH)_2$, is used by silversmiths in preference to chalk.

Rouge is usually composed of extremely fine iron oxide derived from ochre or other ferruginous minerals, or from soluble iron salts by precipitation. The material is afterwards ignited, and the finest particles are then separated by levigation. There are several reactions in which finely divided iron oxide is a by-product, and these serve as further sources of supply. The finest rouge of all—

that employed for the complexion—is prepared from safflowers (*Carthamus tinctoris*) by pulverising them with a solution of carbonate of soda, and subsequently neutralising this with dilute acetic acid. The precipitated rouge is allowed to fall on absorbent cotton. The rouge is removed, subjected to a fresh treatment with soda and placed in a vessel containing very fine talc. On the addition of dilute citric or acetic acid, the colouring matter is again precipitated and collects on the talc. The product is ground by hand with olive oil so as to ensure the desired mellowness.

Rouge is chiefly employed in giving the final polish to metals, its softness and freedom from grit making it specially suitable for this purpose. The red colour of the material also imparts a pleasing tinge to metals polished by its aid; for this reason it is often mixed with chalk in the preparation of plate powders. The cost of rouge is such that it is only employed where a cheaper abrasive will not give the desired result.

Tripoli powder or **rottenstone** is an alumino-silicate of variable composition or even a number of alumino-silicates which happen to be suitable as abrasives and polishes.

The best quality comes from Corfu and is infusorial like kieselguhr, but little notice is now taken of the source so long as the material is satisfactory. A variety of tripoli powder termed **rottenstone** is found at Bakewell in Derbyshire; it is a highly aluminous and very soft rock, and owes its brown colour to the iron it contains.

Kieselguhr is a fine siliceous powder composed of the sheaths of minute diatoms and is one of the best known forms of diatomaceous earth. Like other forms of exceedingly finely powdered or levigated silica, it is largely used as the abrasive in pastes and liquids for polishing metals and wood. For this purpose it must be free from all gritty particles.

Pumice stone is a product of volcanic action, and is therefore found in the neighbourhood of volcanoes. Large quantities of it are obtained from Rhenish Prussia.

It is a more powerful abrasive than the other mild ones just mentioned, and is largely used as a preliminary polisher in cases where a quick-acting abrasive is required, but where sand or the harder abrasives would be unsuitable. It is also mixed with soap to increase the detergent properties of the latter.

Abrasives for dentifrices, usually consist of air-floated silica, china-clay, chalk or other mild mineral or synthetic abrasives; it is essential that the particles in them shall be extremely small, moderately yet not sharply angular and of fairly uniform size.

Abrasive papers and cloths are made as follows:—

Abrasive cloths and papers are usually coated with emery, quartz (see *glass paper*) garnets (chiefly for woodworking) silicon carbide ("carborundum") or corundum.

First the stock passes between circular rolls which print on one side the name of the company, the kind of abrasive used, and its number; it then passes between two rubber rolls, the lower one of which is immersed in a tank of hot glue. The coat of glue, which is deposited on one side, is next spread evenly by a narrow brush which extends across the stock, and has a very rapid reciprocating movement. Just beyond the brush there is a hopper, from which an even stream of abrasive falls upon the stock; the latter then passes under a steel roll, which forces or imbeds the abrasive grains into the glue, holding them firmly on the stock.

The paper or cloth next passes over an elevated drum, and is then gathered up into loops about 12 ft. long by an endless-chain mechanism, which at regular intervals carries a wooden cross-bar up under the sheet as it feeds out. When one of these sticks upon which one of the loops is suspended is conveyed to the top, it enters upon a horizontal track and is conveyed along by a slow intermittent motion so that the first coat of glue will have time to partially dry before the next coating operation. This intermittent motion is obtained from a framework that extends above the track and moves back and forth. The stroke of this frame is about 12 in., and with each forward movement pawls on it engage the cross-bars upon which the loops hang and push them forward a distance equal to the stroke of the frame. On the return stroke the pawls simply lift and glide back over the sticks, and then engage another set on the next stroke. As the result of this intermittent movement, the loops of cloth or paper swing to and fro as they gradually move along, presenting a rather grotesque appearance.

About one hundred feet from the starting point, the paper which has partly dried passes through a second glue-coating process. This is known as "sizing." The glue is much thinner than is used for the first coat, and is applied to fill up the interstices between the abrasive grains and hold them more firmly in place. When one of the loops approaches this second or sizing machine, it is straightened out as the paper is drawn between the tensioning and glueing rolls, and this straightening out draws the loop cross-bar (which has passed beyond the feeding pawls) forward, and the cross-bar drops upon conveyer chains, and is lowered to the floor.

The paper, after passing the point where the cross-bar support is removed, is drawn over a curved platform down to the tensioning rolls, and then to the second set of glueing rolls. After the sizing operation, the paper passes over a drum or roll on the periphery of which are raised strips that incline from each side towards the centre, similar to the teeth of a herring-bone gear. This roll is to centre the paper before it again enters upon the drying track. The paper is now gathered up into loops upon cross-bars which are automatically elevated at proper intervals, the arrangement being the same as that used after the first coating process.

The loops of coated paper now begin a long journey which continues in a straight line to the end of the room, the motion being intermittent and effected by the feed-pawl mechanism previously referred to. When the procession of swinging loops reaches the end of the room it makes a short turn on a curved track, and proceeds back in the opposite direction. The feed of the cross-bars around this curved end is obtained by a pawl-feeding mechanism similar to that described, except that it is curved to conform to the track, and this curved, fan-shaped frame has an oscillating movement instead of a straight-line motion.

After passing the curve, the loops, which hang quite close together, travel in an unbroken line and on a continuous track from one end of the building to the other several times. At the end of the last track the supporting cross-bars fall on to another chain conveyer, and are carried down to the floor. The stock is then drawn over another curved platform, just beyond which there is a series of rolls which iron out the wrinkles and also provide tension preparatory to winding the coated stock on to an arbor. This is the end of the coating operation.

The complete passage from the first coating rolls to the end where the coated and dried stock is wound on to rolls requires several hours. When the tracks are completely filled with paper they hold a continuous sheet (joined by glue where breaks have occurred, or where a new roll of paper has been started) which, if straightened out, would extend about eleven miles.

The coating process is practically the same for cloth as for paper, except that the cloth stock requires two passages through the coating machine, one for coating with glue and another for coating with both glue and abrasive. A preliminary coat of glue is necessary, because the cloth absorbs more glue than the paper. Stock varying from 18–48 in. wide can be run through this coating machine. When a lot of paper or cloth is to be coated, the wide stock is put through first, the order being from wide to narrow. This is done so that any wear might occur on the rubber glue-coating rolls will not affect the narrower widths. Similarly, stock requiring the coarse abrasives is coated last, the order being from fine to coarse to avoid any possibility of coarse grains which might have remained in the machine being deposited upon a paper of finer grain.

The large rolls of coated stock are cut into various shapes in another department.

Glass paper is seldom made with glass, quartz grains being harder and more satisfactory.

POLISHES

Polishes are of two kinds: those which rub away the surface of the material until a smooth and polished surface is obtained and those which cover the material with a coating which is, in itself, smooth and reflective. The former kinds of polish are abrasives and have been described in the pages immediately preceding; the latter are more in the nature of varnishes and lacquers, but differ from these in several marked respects (see **Martin's** "Industrial Chemistry: Organic") and partake rather of the nature of oils and waxes (*ibid.*).

Polishes may be required chiefly to restore a bright surface which has become dull on exposure, and, in the case of metals, has become covered with a film of oxide which makes it tarnished. The object of the polish is to remove this tarnish, whilst at the same time removing as little of the metal as possible. This may be effected by the process known as **buffing,** which consists in holding the article against a rapidly rotating disc of cloth charged with a mild abrasive, such as lime or chalk; but useful as is this method for the manufacturer, it would be too strong for the owners of the finished goods and would wear away the surface too rapidly if frequently repeated. The abrasive is therefore applied with a piece of flannel and is rubbed by hand on to the object to be polished, the surface being afterwards finished with a wash-leather (chamois leather) or (in the "trade") by rubbing with the fleshy part of the palm, this latter being superior to any other polishing medium for giving the final polish to metals.

It is not always necessary to use an abrasive of a solid nature; thus ammonia solution applied with a piece of flannel will frequently renew the polish on tarnished metals, and paraffin is a well-known remover of rust. Most **metal polishes** contain both solid and liquid abrasives and a detergent, the best known ones consisting of soap, oil, whiting, chalk, or finely levigated silica, and a colouring agent. Some of the much advertised brass polishes contain finely-ground and air-floated tripoli powder or other form of silica as the chief solid abrasive, with oxalic acid or a modern detergent of the sulphonated hydrocarbon type to loosen the tarnish, and paraffin as the chief liquid or "vehicle".

There are two kinds of polish on metals; one is known as "colour" and is almost a mirror-like polish, in which all the grain of the metal has disappeared. It is seen on high-class steam fittings, etc., and is produced by holding the work against bobs or mops of felt or calico charged with a mild abrasive such as whiting or lime, though it may be produced on work running in the lathe, if the finest abrasive cloth or paper is used and followed with a piece of wash-leather charged with metal polish.

The other kind of polished surface is seen on scientific instruments and is known as **mathematical grain.** It is somewhat difficult to describe its exact appearance, but if an astronomical telescope, photographic lens, or microscope is carefully examined, it will be seen that there is a certain amount of grain under the polish. This is obtained by the use of planishing and burnishing tools, the metal being subsequently covered with lacquer such as those described in **Martin's** "Industrial Chemistry: Organic."

Stove polishes are of several kinds. The one chiefly used some years ago, under the name of **blacklead,** consisted of finely ground graphite—a form of the element carbon which occurs as a mineral in Cumberland, Ceylon, and elsewhere. **Brunswick black** consists of asphaltum or pitch mixed with turpentine and linseed oil and heated until the mixture becomes uniform throughout, but some of the preparations sold as Brunswick black contain benzoline or other hydrocarbon vehicles, and the pigment is bone pitch or some other convenient form of carbon instead of asphaltum or bitumen. Some modern stove polishes are solutions of anilin black and cellulose in acetone or other solvent.

Furniture polishes consist chiefly of beeswax, paraffin wax, carnauba or other waxes, soap, turpentine, alcohol, and water, made into an emulsion, but some consist of a solution of sandarc and shellac (with or without gums) in alcohol, and others of a solution of celluloid in acetone or other solvent.

French polish for woodwork consists of shellac dissolved in alcohol and coloured with "dragon's blood." Various other gums, such as benzoin and juniper, are also added by some polishers.

The proportions vary very greatly, and are apparently adapted to suit the skill of the workman rather than to secure the best result apart from any question of skill in application.

Boot and shoe polishes vary greatly in composition, but their essential constituents are shellac, wax, lampblack or an aniline black or light brown dye, with turpentine, paraffin, or alcohol as a vehicle. Too much shellac must not be used or the polish will crack. Spermaceti is used to prevent this in some polishes. To prevent the paste from drying to an inconvenient powder, a little glycerine may be added with advantage.

Boot and shoe polishes are more conveniently considered under **Waxes** (**Martin's** "Industrial Chemistry: Organic").

Boot blackings consist of bone-black, sugar syrup, sulphuric acid, and olive oil, or their equivalents.

Mechanical methods of polishing are very various, each industry employing its own adaptations of the general methods. In most cases they consist in applying the abrasive or waxy polish to the article under a considerable pressure, this being applied by hand or mechanically, according to the nature of the material to be polished. Thus, wood polishers work entirely by hand, but in the polishing of stones, lenses, and metals the earlier stages are all carried out mechanically—usually by rotating a disc carrying the abrasive and applying the object to be polished to this, or by making the object rotate and applying the abrasive to it under the pressure of a metal or wooden polishing tool. The final stages may be assisted by the use of mechanism, but the pressure to be applied is usually so slight that it must be applied by the hand of a skilled operative.

Many improvements in polishes have been made in recent years, the nature of most of these is regarded as a trade secret or is protected by patents. The improvements consist chiefly in the use of a blend of several waxes (instead of only one wax) and in the use of many solvents and vehicles not previously available, for example silicon fluids.

SECTION LXXXVIII

PHOSPHORUS

By C. Ainsworth Mitchell, B.A. (Oxon.), F.I.C.
Revised by Wilfrid Francis

Phosphorus, in combination with other elements, is one of the most abundant substances in nature. In the form of calcium phosphate it is the principal constituent of various minerals such as phosphorite and apatite; in others it is present as iron phosphate, aluminium phosphate, etc. It is also a chief constituent of the bones of vertebrate animals, and is found in the brain substance, muscles, etc.

It was discovered towards the close of the seventeenth century by Brand, who had ignited the residue left on the evaporation of urine in a search for the philosopher's stone; and in 1755 it was prepared by Scheele by the distillation of bones.

Until comparatively recently modifications of this method were still the only manufacturing processes.

By dry distillation of bones in iron retorts, a distillate known as **Dippel's animal oil** is obtained, while a residue of **bone charcoal** or **bone earth** is left behind. This bone charcoal, after being used as a decolorising agent in sugar refineries, is calcined to obtain **bone ash,** which was formerly obtained by directly calcining the bones in kilns.

This bone ash is washed in leaden tanks, first with hot water, and then with the calculated amount of sulphuric acid to convert the tricalcium phosphate in the ash into the soluble monocalcium salts—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

After dilution and sedimentation of the calcium sulphate the clear phosphate solution is decanted, and concentrated in leaden pans to a specific gravity of 1.45, after which it is mixed with a little wood charcoal, and evaporated to a nearly dry solid mass in iron pans.

This residue is next heated in horizontal terra-cotta retorts, arranged back to back in rows in a furnace, and after being exposed to red heat for twenty-four hours the monocalcium phosphate is converted into calcium metaphosphate—

$$CaH_4(PO_4)_2 = 2H_2O + Ca(PO_3)_2.$$

The temperature is then raised to white heat for about forty-six hours, with the result that tricalcium phosphate is produced, while carbon monoxide is evolved, and free phosphorus distils—

$$3Ca(PO_3)_2 + 10C = 10CO + Ca_3(PO_4)_2 + P_4.$$

The phosphorus is condensed under water, and is purified by redistillation with a small proportion of moist sand, and is finally moulded into cylinders under water.

Another method of purification used in France is to treat the phosphorus under warm water with sulphuric acid and potassium bichromate.

The drawbacks to this process, apart from the cost of the raw material, are th it only yields a portion of the phosphorus present, and that compounds of pho phorus and sulphur are simultaneously produced, and have subsequently to b eliminated. Hence the final yield of the pure product is less than 10 per cent. of th original material.

In Fleck's process, now abandoned, hydrochloric acid was used instead o sulphuric acid for the decomposition of the bone ash.

Wöhler (*Pflüg. Arch.*, XVII., 170) devised a process for obtaining a better yiel of phosphorus by heating the slightly charred bones with sand—

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 7CaSiO_3 + 10CO + P_4,$$

but it was found that high temperatures were required, and that the calcium silicat attacked the retorts to such an extent as to render the process unpracticable on a manufacturing scale. For the same reason the process could not be used for the treatment of mineral phosphates.

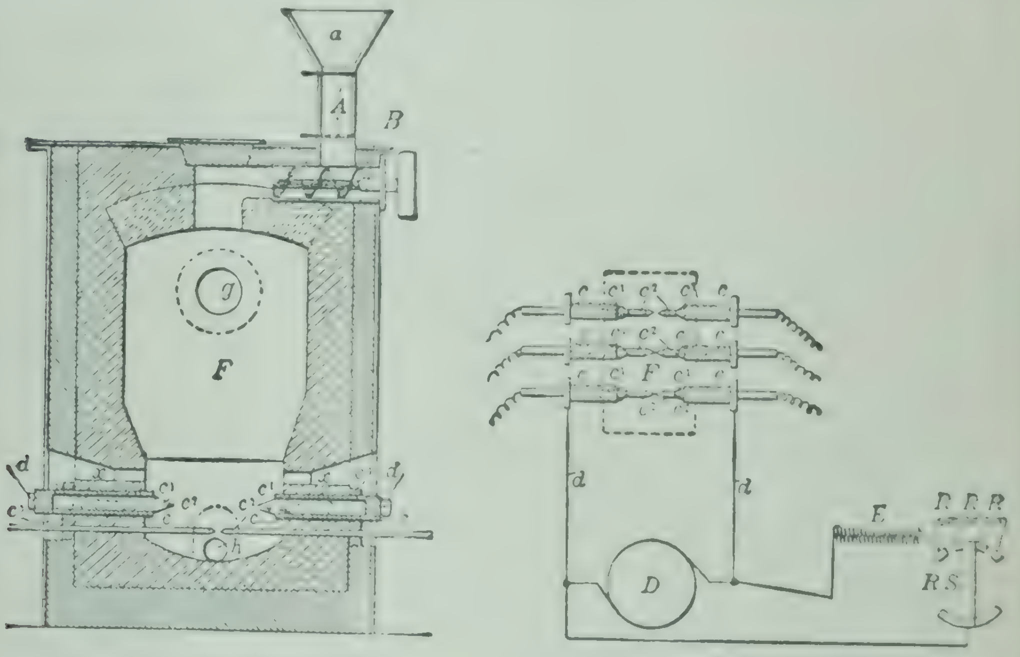


Fig. 1.—Vertical Section. **Fig. 2.**—Arrangement of Electrodes.
Readman and Parker's Phosphorus Furnace.

Readman and Parker's Process. It was not until an electric furnace was used for heating the mixture (1868) that it was found possible to prepare phosphorus by Wöhler's process. Readman and Parker's furnace is shown in Figs. 1 and 2.

A finely ground mixture of 100 parts of phosphorite with 50 parts of sand and 50 parts of charcoal is introduced into the hopper *a*.

After the initial heating has been effected by a current passing through the movable carbons c^2, the latter are withdrawn, and an arc light made to pass between the electrodes c^1. The phosphorus fumes pass through the tube *g*, and are co densed in water contained in copper receivers.

Any oxidation of the phosphorus may be prevented by passing a current of coal gas through the retort.

In the furnace of the Electric Reduction Co. (Fig. 3) the mixture of phosphate, carbon, and silica is placed on a bed E, beneath a rod of graphite D of high resistance connecting the two blocks of carbon B. On transmitting a current the rod D becomes white hot, and the deflected heat decomposes the phosphate mixture. The phosphorus fumes escape through the tube F to the condensers, while the slag is afterwards removed through the outlet G.

To prevent decomposition of the water in the condensers by the phosphorus vapours the Compagnie Électrique du Phosphore, Billaudot et Cie, have patented (German Patent, 106,498) a process whereby the condensation is effected in an atmosphere of carbon monoxide which is formed in the reaction.

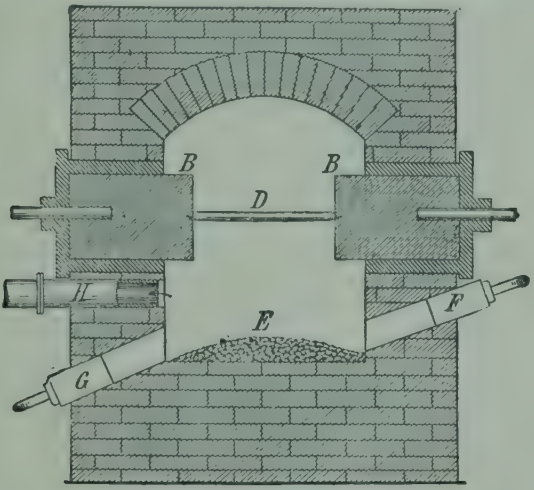


Fig. 3.—Phosphorus Furnace of the Electric Reduction Co.

A diagram of their furnace is shown in Fig. 4. The vapours (namely, phosphorus and carbon monoxide) formed in the furnace F are freed from solid particles by passing through the tube *a*. Thence they pass through D and the upright tubes T, which are kept at 50° C., into the tube E, where the bulk of the phosphorus condenses and falls into D. The regulation of the temperature and the speed of the passage of the vapours is controlled by a current of carbon monoxide, which is stored in R and can be forced through the openings *t* in the tubes T. Any phosphorus escaping uncondensed from E passes onwards into the tower G, where it is brought into intimate contact with a solution of copper sulphate. The resulting copper phosphide is used in the manufacture of phosphor bronze.

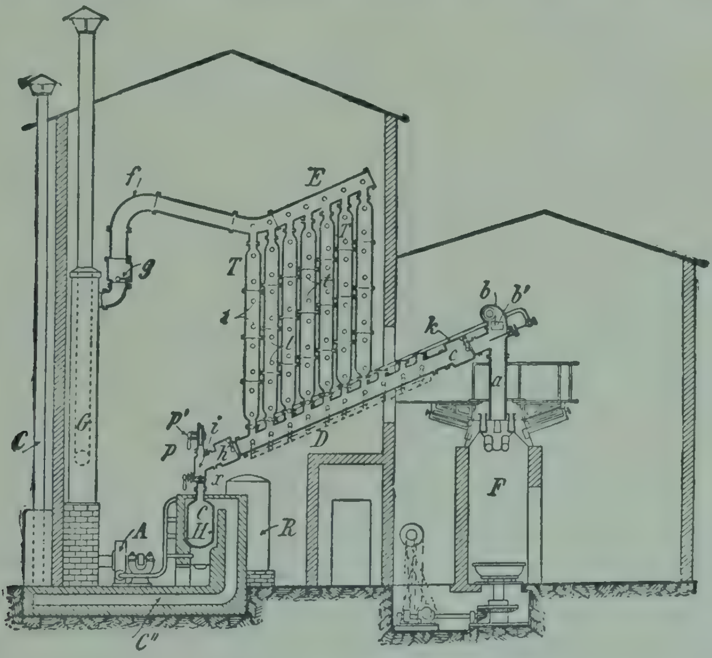


Fig. 4.—Phosphorus Condensation Plant of the Compagnie Électrique du Phosphore, Billaudot et Cie.

The electrical methods of producing phosphorus are everywhere taking the place of the old method of distilling bones, for the high temperatures required for the reaction (1,300°–1,450° C.) are in this way most economically obtained. The residual slags still contain about 20 per cent. of the phosphorus originally present. This is left in the form of irreducible iron phosphide or silico-phosphoric acid.

In **Neumann's process** (*Zeit. angew. Chem.*, XCV., 291) a better yield of phosphorus is obtained by reducing phosphoric acid with carbon at a temperature of 650°–850° C.—

$$2HPO_3 + 5C = 2P + 5CO + H_2O.$$

Earthenware retorts are used for this purpose, and lower grades of phosphorite may be used as the raw material.

Harding's process is based upon a similar reaction. Phosphorite is first decomposed with an excess of sulphuric acid, and the phosphoric acid solution filtered from calcium sulphate mixed with carbon and evaporated to dryness. It is next heated to expel sulphates, and the residue of phosphoric and phosphorus oxides is reduced in an electric furnace.

The simultaneous production of calcium carbide and phosphorus was the basis of **Hilbert** and **Frank's** German process, and **Bradley** and **Jacobs'** English process.

In **Joudrain's** process, on these lines, the raw material, phosphorite, is heated with an excess of charcoal in carbide furnaces, and the phosphorus fumes condensed in water towers—

$$Ca_3(PO_4)_2 + 14C = 3CaC_2 + P_2 + 8CO.$$

It is doubtful whether the carbide thus produced would be sufficiently pure for ordinary purposes.

Reduction of phosphoric acid or phosphates with metallic zinc or aluminium (Rossel, German Patent, 71,259) in the presence of sand has also been proposed as an industrial method of preparing phosphorus.

PHOSPHORUS

Recent Developments in Production and Uses.—As mentioned in Section LXXXVI, the preparation of yellow phosphorus in the electric furnace has extended rapidly in recent years, so that production in the U.S.A. reached 250,000,000 lb. in 1949. The outlet for much of the phosphorus so produced was in the preparation of phosphoric acid and phosphates in applications where a higher degree of purity is required than is obtainable by the preparation of phosphoric acid by the action of sulphuric acid on phosphate rock. The direct production of phosphoric acid by the combustion of phosphorus is also now largely practised in European countries.

In the American process, operated by the Monsanto Chemical Company, the ore, with a minimum phosphorus content of 25 per cent., is usually some form of apatite, $Ca(F.Cl)_2$, $3Ca_3(PO_4)_2$, as mined in Morocco, Florida, Tennessee, and the Rocky Mountains Province. The ore is sometimes calcined or agglomerated by sintering before reduction, which is carried out at 1,500° C. to 1,600° C. in the presence of silica gravel and coke breeze, sufficient to give a slag with a silica-lime ration of 0.8–0.9. The slag is very corrosive at the operating temperatures and is tapped at intervals of one to two hours. The reaction follows the course of the early process of Wöhler, mentioned on p. 444, viz..

$$2Ca_3(PO_4)_2 + 6S_1O_2 + 10C = 7CaSiO_3 + 10CO + P_4.$$

The furnace used is lined with carbon bricks and has a separate tap hole, below the slag hole, for running off the ferro-phosphorus which is also formed during the process. A layer of ferro-phosphorus is always left at the bottom of the furnace to protect the lining from the action of the slag. The vapour of phosphorus and the carbon-dioxide formed during the reaction leave the furnace through a duct in the roof and pass through electrostatic precipitators operating at above 200° C., so as to precipitate entrained dust without condensing the phosphorus. The cleaned gases then pass to a cooling system of spray towers where the phosphorus condenses as a yellow liquid, and is collected and stored under water. The purity of the yellow phosphorus prepared in this way is 99.9 per cent.

The yield of products obtained varies with the nature of the ore treated, but with a normal apatite, approximately 88 per cent. of the phosphorus is recovered in elemental form; 8 per cent. is recovered as ferro-phosphorus and is sold for metallurgical purposes, whilst 7 per cent. is lost in the slag. The slag is obtained in a granulated form by dropping, whilst molten, into water and may be used as a conditioning medium for heavy clay soils. The power consumption of the reduction furnace varies from 6.5 kWh. to 7.0 kWh. per lb. of phosphorus produced.

Properties.—The so-called **yellow** or **white** phosphorus is a wax-like solid which melts at 44.4° C., boils at 287° C., and has a specific gravity of 1.83. It is insoluble in water, but dissolves readily in carbon bisulphide, and is slightly soluble in alcohol and ether. It "phosphoresces" in the dark, and when exposed to the air in a finely divided state ignites spontaneously.

In Mitscherlich's test for the detection of traces of white phosphorus the substance is boiled with water in the dark, the steam becoming luminous when phosphorus vapours are present.

Phosphorus dissolved in carbon bisulphide will precipitate metallic phosphides from solutions of salts of the metals, as, for example, silver phosphide, PAg_3, and copper phosphide, Cu_3P_2.

White phosphorus is extremely poisonous, and absorption of the vapours causes chronic necrosis of the jaws and teeth.

Allotropic Modifications of Phosphorus.—Several allotropic forms of phosphorus are known, including Schroller's "amorphous" **red** phosphorus discovered in 1845, Hittorf's **violet** phosphorus, Schenk's **scarlet** phosphorus and Bridgman's **black** phosphorus.

Red Phosphorus, which is sometimes also termed **amorphous** phosphorus, though it forms hexagonal crystals, is slowly produced when white phosphorus is exposed to light. It is more rapidly produced by heating ordinary phosphorus in a vacuum at 300° C., or with a trace of iodine at a lower temperature.

On a manufacturing scale it is prepared in Albright's apparatus, which consists of a cast-iron vessel containing an inner porcelain chamber, the top of which can be screwed down. The space between the inner and outer chamber is filled with sand, and the iron vessel also rests upon a sand bath, which is heated for eight days at a temperature of 230°–250° C. From the top of the porcelain chamber containing the soluble phosphorus there passes a bent tube, the end of which dips into a trough of mercury to form a seal.

At the end of the operation a mass of red phosphorus, mixed with unaltered white phosphorus, is left in the chamber. By boiling the mixture with sodium hydroxide solution the white phosphorus is converted into phosphine, PH_3, which escapes, leaving the red phosphorus unaltered.

A more recent method of separating the two varieties is based upon the difference in their specific gravity. The mixture is first finely ground under water, and then incorporated with a solution of calcium chloride of sp. gr. 1.9 at 50° C. The white phosphorus (sp. gr. 1.83–1.84) melts and rises to the surface, while the red phosphorus (sp. gr. 2.1) remains at the bottom. A separation of the two kinds of phosphorus may also be effected by extracting the mixture with carbon bisulphide, in which red phosphorus is insoluble.

Hittorf's Violet Phosphorus.—This is prepared by heating white phosphorus with lead in a sealed tube to a temperature of about 800° C., and subsequently dissolving the lead by means of an electrolytic bath of lead acetate and acetic acid. Metallic bismuth may be used instead of lead in this process, but a lower yield of the black phosphorus is obtained.

The specific gravity of Hittorf's modification is 2.31–2.33. It is more inert than red phosphorus, but oxidises very slowly in the air. Violet phosphorus melts at 620°–625° C.

A so-called **pyromorphic phosphorus** is described by Jolibois (*Comptes Rend.*, 1910, CLI., 382). It is prepared by treating red phosphorus with a trace of iodine at 280° C., or *in vacuo*. It is more stable than red phosphorus at temperatures below 450° C.

Incomplete conversion of red phosphorus into this modification yields a puce-coloured product consisting of a mixture of the two modifications.

When red phosphorus is heated at 725° C. it is converted into a violet modification with a specific gravity of 2.27.

Schenk's Scarlet Phosphorus is obtained by heating a solution of phosphorus in a solvent that acts at the same time as a catalytic agent, *e.g.*, phosphorus tribromide. After several hours at a relatively low temperature (175° C.), the scarlet phosphorus is deposited as an amorphous powder, which is separated from the phosphorus tribromide by boiling it with water. It has the stability of ordinary red phosphorus, but reacts more readily with reagents, and is therefore used in the manufacture of safety matches.

In a process patented by Totenhaupt (German Patent, 171,364) this modification is obtained by heating a solution of white phosphorus in a hydrocarbon such as benzene or naphthalene for several hours at 120° C. in the presence of 0.25–0.5 per cent. of iodine.

In addition to its principal use in the match industry, red phosphorus is used in the preparation of hydriodic acid, and for producing a vacuum in electric lamps.

Bridgman's Black Phosphorus.—According to P. W. Bridgman (*J. Am. Chem. Soc.*, **38**, 609, 1916), yellow phosphorus may be changed into a stable black variety by heating to a temperature of 200° C. at pressures between 12,000–13,000 atmospheres. At lower temperatures and pressures, the red variety is formed. Black phosphorus is a stable allotropic form of phosphorus, insoluble in carbon disulphide and unattacked by cold, concentrated nitric or sulphuric acids. The specific gravity of black phosphorus is 2.69, which compares with 2.05–2.3[illegible] for red phosphorus and 1.83–1.84 for yellow phosphorus.

Colloidal Red Phosphorus.—Colloidal solutions of high viscosity may be obtained by boiling red phosphorus with water containing protective colloids, such as gelatin, albumen, casein, glue, or sucrose. Such solutions are only flocculated with difficulty on the addition of electrolytes.

Colloidal Yellow Phosphorus.—Colloidal solutions of yellow phosphorus may be prepared by pouring a solution of yellow phosphorus in alcohol into a considerable excess of water.

Varieties of Red Phosphorus.—The term "red phosphorus" includes a large number of materials with properties differing according to the method of preparation. Thus, a wide variation in specific gravity between the limits 2.[illegible]5 and 2.39 has been observed, whilst the melting point varies between the limits 600° C. and 615° C. For these reasons Bridgman (*loc. cit.*), and others, consider that red phosphorus is not a single substance, but a transitional product intermediate in composition between yellow phosphorus and violet phosphorus.

Uses for Phosphorus.—The element itself is chiefly used for match making, in the preparation of rat poisons, and the manufacture of phosphor bronze. The phosphates are used as fertilisers, chemical foods, fire-proofing agents for conditioning boiler waters, and for the preparation of rust-proof finishes for sheet steel. Organic phosphates are used as plasticisers and insecticides.

Calcium phosphide (P_2Ca_2), formed by heating calcium phosphate with powdered aluminium, is decomposed by water, forming **phosgene,** phosphine, or hydrogen phosphide (PH_3). The latter is a spontaneously inflammable gas smelling strongly of mixed garlic and decaying fish. These properties are responsible for the two main uses of calcium phosphide, namely as a drain tester and as a flare of sea operations, called the Holmes' signal. In the former application, the leak is detected by the smell of phosphine, whilst in the latter device the phosphine ignites and burns with a bright, luminous flame.

For further details of the use of phosphorus for matches, see Martin, Vol. II, Section LXXXIX. For the use of phosphates as fertilisers, see Section LIV, and for their use in water conditioning, see Vol. I, Section X.

REFERENCES

(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry." Vol. VIII, London, 1947.
(2) C. H. Aall, *Chem. and Ind.*, December 30, 1950.

SECTION LXXXIX

MATCHES

By C. Ainsworth Mitchell, B.A., F.I.C.
Revised by Wilfrid Francis

LITERATURE

Clayton, E. G.—*Proc. Chem. Soc.*, XXVII, 229 (1911).
——*J. Soc. Chem. Ind.*, XXXI, 568 (1912).
C. A. Keane and P. C. L. Thorpe.—"Explosives, Matches, and Fireworks." London, 1938.
J. Missedin.—"The World's Match Industry." *C.T.J.*, August 29, 1924.

Prior to the invention of phosphorus matches early in the nineteenth century, "friction lights" were manufactured by Walker in this country. These consisted of antimony sulphide and potassium chlorate, and were ignited by friction upon sandpaper. "Lucifer" matches of a similar character were invented by Jones.

The following analyses by E. J. Clayton [1] gives the percentage composition of typical specimens of these early matches:—

	S.	KClO$_3$.	Lycopodium.	Gum.	Antimony Sulphide.	Ferric Oxide.
"Promethean" matches[2] (1828) -	24.7	34.9	8.8	31.6	...	...
"Lucifer" ,, I. (1832-3)	6.5	27.6	...	35.7	24.6	5.6
"Lucifer" ,, II. (1832-3)	12.5	41.0	...	24.9	18.1	3.3

The earliest phosphorus matches made in France, Germany, and Austria contained potassium chlorate, and owing to the danger attending their use were soon prohibited in the latter countries. They were imported in large quantities into England.

Typical examples of early phosphorus matches, examined by Clayton, had the following percentage composition:—

	Ordinary Phosphorus.	S.	KClO$_3$.	Chalk.	Dextrin.	Gum.	Dye.
German (about 1835)	20.5	14.3	32.1	8.0	25.1	...	Trace of blue dye.
Austrian (1835-50) -	17.8	11.5	37.4	...	...	33.3	...

In 1837 matches were made in Germany in which the potassium chlorate was replaced by the product of the interaction of red lead and nitric acid. The first "safety" matches were invented by Böttger in 1843, the composition of these being ignited by friction upon a surface coated with red phosphorus.

---

[1] *Proc. Chem. Soc.*, 1911, XXVII, 229.
[2] Ignited by dilute sulphuric acid, coloured with indigo.

Matches of a similar kind were soon afterwards manufactured in Sweden, but for many years could not compete commercially with matches containing white phosphorus.

Composition of White Phosphorus Matches.—The heads on these usually contain from 4.7 per cent. of ordinary white phosphorus mixed with an oxidising agent such as lead oxide.

The various ingredients are heated together in a closed vessel over hot water, and are meanwhile continually stirred with an agitator. The wooden spills are dipped into this paste, then dried in a current of air, and their heads finally coated with a thin layer of varnish.

Jettel gives the following formula as typical :—Water, 4.5 litres; glue, 2 kilos; glass powder, 2 kilos; iron oxide, 0.5 kilo; cinnabar, 0.1 kilo; and white phosphorus, 2.5 kilos.

Safety Match Compositions.—These consist, in the main, of potassium chlorate and sulphur, or a similar substance, with additions to reduce the violence of the ignition. They are ignited upon a surface coated with a mixture of red phosphorus, antimony sulphide, and powdered glass.

Ichenhaüser gives the following representative formula:—

Potassium chlorate, 18; potassium bichromate, 1.6; sulphur, 0.4; manganese dioxide, 1.8; iron oxide, 1; umber, 1; glass powder, 2; glue, 1; and gum arabic, 4 kilos.

The accompanying striking surface consists of red phosphorus, 1.0; antimony trisulphide, 0.25; lampblack, 0.50; and dextrin, 0.30 kilos.

The splints for the matches are prepared from non-resinous woods, generally aspen wood, large quantities of which are exported from Russia. They are impregnated with paraffin wax before being tipped with the composition.

Resinous woods are also sometimes used after treatment with sodium carbonate solution (Hälwe's German Patent, 130,919), or with phosphoric acid solution (Benedick's German Patent, 144,229).

After-glowing is prevented by impregnating the woods with a solution of phosphoric acid and ammonium phosphate.

Prohibition of White Phosphorus Matches.—In 1906 a Conference was held at Berne at which most of the principal nations of Europe agreed to prohibit the sale and export of matches containing white phosphorus. Some countries, however, including Great Britain, Belgium, Russia, and the United States, were unable to agree to the prohibition, and relied upon measures to prevent the occurrence of necrosis in the works.

In this country these still proved ineffectual, and in 1908 the White Phosphorus in Matches Prohibition Act was passed, and came into force on 1st January 1910.

In the United States the so-called "**double-dip**" matches, which contained from 14-20 per cent. of white phosphorus, were in great demand owing to the readiness with which they ignited; but in that country too an Act in 1912 was passed prohibiting their sale and export after January 1914, and imposing a tax upon white phosphorus matches sold after July 1913.

A method of detecting white phosphorus in match composition is described by Thorpe (*Chem. Soc. Proc.*, 1909, XXVI., 73). The substance is greatly heated *in vacuo*, and the white phosphorus, which sublimes under these conditions, is then identified by its physical properties.

Substitutes for White Phosphorus.—The substances used as substitutes for white phosphorus in match compositions include amorphous red phosphorus and other allotropic modifications, hydrides, oxides, and sulphides of phosphorus mixed with potassium chlorate or other oxygenating substance, and with inert substances to reduce the violence of the ignition.

USE OF PHOSPHORUS SULPHIDES

French State Matches.—These are made by the process of Sévène and Cahen, with a composition consisting essentially of phosphorus sesqui-sulphide, P_4S_3, and potassium chlorate, with other ingredients in approximately the following proportions:—Phosphorus sesqui-sulphide, 6; potassium chlorate, 24; zinc white, 6; red ochre, 6; powdered glass, 6; glue, 18; and water, 34 parts.

They are liable to slow decomposition in moist air, with the liberation of hydrogen sulphide.

The use of other phosphorous sulphides, P_3S_6, is claimed by the Griesheim-Elektron Chemical Co. (German Patent, No. 163,078), whilst Huch (German Patent, No. 174,878) has protected a composition containing a brown powder (16 per cent. of S and 82 per cent. of P) produced by the interaction of sulphur chloride and red phosphorus.

A phosphorus polysulphide, P_4S_{10}, claimed in German Patent, 239,162, and French Patent, 424,522, of 1910, has been shown by Stock and Frederici (*Zeit. angew. Chem.*, 1912, XXV., 2201) to be mainly a mixture of sulphur and the sulphide P_4S_3. Thiophosphites made by heating sulphides (*e.g.*, Sb_2S_3, ZnS, etc.) with red phosphorus and sulphur in an atmosphere of carbon dioxide to a temperature of 450° C. are used in compositions patented by the Elektron Fabrik (German Patent, No. 153,188), as for example in the formula:—Zinc thiophosphite, 30; potassium chlorate, 60; zinc oxide, 5; gypsum, 3; chalk 5; and powdered glass, 10 parts.

Matches of this composition are less affected by moisture than those containing phosphorus sulphides.

Various allotropic modifications of phosphorus, such as Schenk's scarlet phosphorus and Hittorf's variety (*Ber.*, 1909, XLII., 4510), which is obtained by heating phosphorus with lead in closed tubes to a high temperature, are also used for match compositions.

An ignition composition claimed by G. W. Johnson (English Patent, 21,931, of 1909) contains the following ingredients:—Red phosphorus, 350; antimony pentasulphide, 400; chalk, 100; zinc oxide, 100; and powdered glass, 100 parts.

These are made into a paste with water, and incorporated with:—Glue, 500; potassium chlorate, 1,300; chalk, 50; zinc oxide, 50; and powdered glass, 50 parts.

A paste upon somewhat similar lines is claimed by Caussemille Jeune et Cie et Roche (French Patent, 404,337, of 1909), the phosphorus therein being described as "neutral amorphous phosphorus," obtained from ordinary phosphorus by distillation and filtration.

The preparation and properties of two solid hydrogen phosphides, $P_{12}H_6$ and P_9H_2, are described by Stock, Bottcher, and Lenger (*Ber. d. d. Chem. Ges.*, 1909, XLII., 2839). The orange-coloured compound, P_9H_2, is used in a match composition patented by Wheelwright (English Patents, 21,866, of 1906, and 3,214, of 1910).

MATCH MANUFACTURE

In the early days of hand manufacture, individual splinters of wood were dipped in the match head composition. In the modern match manufacture, the operations are entirely mechanical and machines are available that are capable of producing 10,000,000 matches per day. The wood for the matches is usually carefully prepared from selected blocks of pine or aspen. Planks are first cut up into 2 in. thick blocks, seasoned for about two years, and then cut up again into smaller blocks, free from knots, for feeding into the splint-making machine. In America the splints are cut by forcing the blocks through grooved dies, whilst in England the splints are cut, with a square section, by means of circular knives. The splints are then impregnated with a fire-resisting solution to prevent afterglow when the match is extinguished. The solution usually contains boric acid or ammonium phosphate.

After drying, the splints, with one end fixed in the perforations of cast iron or steel plates, are carried forward on an endless chain, first to a paraffin wax bath and thence to the vessel containing the striking composition. After drying by hot air, the matches return to the head of the machine, where they are punched of the holes of the plates and into the match boxes, for the final operation of packing.

SECTION XC

ATOMIC POWER

By Norbert Berkowitz

LITERATURE

H. D. Smyth.—"Atomic Energy: general account of the development of methods of using atomic energy for military purposes under the auspices of the U.S. Government." H.M.S.O., London, 1945.

M. Benedict and C. Williams.—"Engineering Developments in the Gaseous Diffusion Process." McGraw-Hill Book Co. Inc., New York, 1949.

Chem. Inst. of Canada.—*Proceedings* of Conference on Nuclear Chemistry. McMaster Univ., Hamilton, Canada, 1947.

G. T. Seaborg, J. J. Katz, and W. M. Manning.—"The Transuranic Elements." McGraw-Hill Book Co. Inc., New York, 1949.

U.S. Atomic Energy Commission.—Technical Information Division: Documents released by the Commission up to January 1950.

A. A. Liebow, S. Warren, and E. DeCoursey.—"Pathology of Atomic Bomb Casualties." *Amer. J. Path.*, **25**, 853 (1949).

E. P. Cronkite.—"Atomic Medicine." Ed. by C. T. Behrens, Atomic Defence Division U.S. Navy (New York).

Sir J. Cockroft.—"The Development and Future of Nuclear Energy." 1950 Romanes Lecture. Oxford Univ. Press.

Penguin Books Ltd.—*Science News*, Vol. II, 1947.

J. A. DeMent and H. C. Dake.—"Uranium and Atomic Power." Chem. Publ. Co. Inc. New York, 1950.

In an attempt to "synthesise" elements heavier than uranium (*i.e.*, so-called "transuranic" elements) by bombarding uranium with neutrons, I. Curie and P. Savitch (1938) observed that the half-life decay period of one of the products of this bombardment resembled that of radio-lanthanum. This observation was confirmed by O. Hahn and F. Strassmann (1939), who reported products with atomic numbers lying between 35 (bromine) and 57 (lanthanum), and L. Meitner (1939) accordingly suggested that after taking up one neutron, the uranium nucleus becomes so unstable that it breaks up immediately into two, approximately equal, fractions.

This phenomenon, which represented a complete departure from previously observed behaviour, at once attracted the attention of leading physicists in Britain, France, and the U.S.A., and led within a few months to several important discoveries. The most important of these was that fission is due primarily to the U-235 isotope (amounting to some 0.7 per cent. of natural uranium). U-238 tends to *capture* neutrons and to become transformed via an unstable U-239 isotope and Neptunium into a relatively stable end-product known as **Plutonium**. This transformation takes the form:—

$$^{238}_{92}\mathrm{U} + ^{1}_{0}n \longrightarrow ^{239}_{92}\mathrm{U} \longrightarrow ^{239}_{93}\mathrm{Np} + ^{0}_{-1}e$$

$$^{239}_{93}\mathrm{Np} \longrightarrow ^{239}_{94}\mathrm{Pu} + ^{0}_{-1}e$$

The half-life periods involved in the transformation are

U-239	23 minutes.
Neptunium	2.3 days.
Plutonium	24,000 years.

It was also demonstrated that slow or "thermal" neutrons had a greater probability of causing fission of U–235 than fast neutrons and that the fission of U–235 was accompanied by an enormous energy release (about 200 million electron volts); and by the emission of two fast *secondary* neutrons.

Since the energy release per gram of U–235 is equivalent to about 2×10^{10} calories (or 10 million kilowatt-hours per lb.), and since the fission is theoretically a self-sustaining reaction owing to the ejection of the secondary neutrons, it was immediately realised that the process could—if controlled—provide a source of relatively cheap power for industrial purposes.

Up to the time of writing (1950), this control has not been achieved on a large scale. Since 1945, however, very extensive research programmes have been initiated (notably in Britain[1] and the U.S.A.) and considerable progress has been made. At the time of going to press (1953), the Ministry of Supply has announced that the world's first atomic power station is to be built on farmland at Calder Hall, near Sellafield, Cumberland.

The Principle of Atomic Power "Piles."—In order to utilise the nuclear energy released by the fission process for industrial purposes, two conditions must be fulfilled: the fast secondary neutrons ejected from the U-235 isotope must be slowed down by some suitable "moderator," and the fission itself must be controlled at a level at which it remains a self-sustaining chain reaction without developing into an "avalanche" or *explosive* reaction.

In practice this is now done by inserting aluminium-sheathed uranium or uranium oxide slugs (containing either the separated U-235, or a mixture of U–235 and 238 respectively) in a graphite block of great purity, and controlling the course of the reaction by the dimensions and spacings of the pile and by adjustable cadmium (or boron) rods. Since graphite acts as a moderator (see below) and cadmium (or boron) as an efficient neutron absorber, the neutron intensity and velocity can thus be controlled independently. The heat released by the reaction is then transmitted to cooling water, which is continuously circulated through the pile, and the reaction is allowed to proceed until all U–235 has been used up, or until the equilibrium amount of plutonium has been formed from the U–238. In the latter case, present practice is to remove the uranium-plutonium slugs from the pile as soon as the reaction begins to slow down, and to separate the plutonium by an acid treatment. Since plutonium is itself a highly fissionable material, it can then be used in place of U–235.

It should, however, be noted that at the present time, when work is concentrated on gaining operational experience rather than on producing power on a large scale, pile-design details vary greatly. For example, if the emphasis is on power production, a so-called "slow neutron reactor" is used, and neutron velocity decreased to such an extent that fission occurs more frequently than capture of neutrons to form U–239 (and subsequently plutonium). This can be done either by paying careful attention to the dimensions of the moderator units, or by using concentrated fissionable material. In the former case, the slugs consist of natural uranium, and in the latter case, either of plutonium or of material heavily enriched in U–235 by isotope separation methods (*cf.* Section LXXXV).

On the other hand, if emphasis is placed on the production of plutonium, the conditions are reversed, and neutron velocity is maintained at such a level that neutron capture becomes relatively more important than fission. A proviso is, of course, that there is a sufficient supply of fissionable material in the pile to maintain a chain reaction. If this is fulfilled, the bulk of the charge is converted into U–239 and thence, via neptunium, into plutonium. It is interesting to note that the first pile specifically designed for this purpose (known as the Clinton pile) was built in 1943 at Oak Ridge, Tennessee. Its power output by June 1944 amounted to more than 1,800 kilowatts. Other piles of this type, generally known as "breeder" piles, are at present under construction in the U.S.A.

---

[1] In Britain, fundamental research into "atomic" energy (more properly, "nuclear" energy) is concentrated at Harwell where two piles (known as the GLEEP and BEPO respectively) are now in operation. Technological work is carried on in at least four other stations in Cheshire and Lancashire, but few details relating to these have so far been released.

The two examples just quoted are only two of a possible series of piles. It is, for instance, quite possible to combine fission and neutron capture (*i.e.*, power generation and "breeding" of Plutonium) in such a way that the reactor "burns" U–235 but at the same time converts U–238 into plutonium. Under such conditions, the reaction is continued with plutonium until virtually all the uranium charged into the pile is used up. Such piles have (like "breeder" piles) a considerably longer life than other reactors, but since they can only function if the number of effective neutrons generated by each fission is greater than 2 * they require particularly careful design. Thus, care must be taken not to introduce excessive amounts of neutron absorbers, and the pile must be made sufficiently large to minimise leakage of neutrons to the exterior. In consequence, the weight of such a pile (inclusive of shielding) may amount to several thousand tons.

Another important difficulty, however, attaches to the operation of these, and other "continuous," piles. By the time a sufficient quantity of plutonium has been formed, the moderator will normally have become poisoned by the fission by-products, and the neutron intensity reduced to a level at which the reaction ceases to be self-sustaining. One must therefore either begin the reaction with extremely pure moderators, or resort to separation of the plutonium and its transfer to another pile.

The importance of the purity of the moderator is well demonstrated by the experience gained at Columbia University in 1941 and 1942. The first reactor there, built with commercial grades of uranium oxide and graphite, gave a reproduction factor of 0.87 (see below*), and a chain-reaction (*i.e.*, a reproduction factor greater than 1) only became possible when the Chicago Metallurgical Laboratory had succeeded in producing pure graphite for the pile.

Neutron Moderators.—Neutrons ejected from U-235 during fission are fast neutrons with an average velocity of about 10^9 cm. per second and must, if they are to be effective in fission processes, be slowed down to about 2.5×10^5 cm. per second (*i.e.*, to the average velocity of neutrons that are moving owing to the thermal agitation produced by a temperature of 20° C.). This slowing down is effected by the "moderator" with which the neutrons can collide elastically (Fermi, 1935). With each collision, some of the energy initially possessed by the neutron is then lost to the atoms of the moderator, and the process stops only when the neutrons have been slowed down to thermal energies. After this has occurred, a neutron may *gain* energy by collisions just as often as it may lose energy.

The best moderators are media containing light elements (*cf.* Table 1). Thus, hydrogen—or more practically, hydrogeneous substances such as water or paraffin wax—slow down neutrons more rapidly than any other substance. Unfortunately, however, hydrogen tends to *capture* thermal *neutrons*, and it does not appear possible to construct uranium-water piles in which the reproduction factor can exceed unity.

Deuterium, particularly in the form of "heavy water" (or deuterium oxide) is more suitable and has actually been used as a moderator in a chain reactor built at the Argonne Laboratory in Chicago. It is, however, an expensive substance, and has for this reason generally been replaced by graphite.

---

* It will be evident that this factor can be reduced to just greater than unity as the reaction approaches completion.

Light elements occupying positions between deuterium and carbon are all unsuitable. Helium (though having a low neutron capture) is not available in a sufficiently dense form; lithium and boron both capture strongly; and beryllium is excluded on the grounds of high cost.

Attempts are now being made to produce pure **carbon** in an effort to replace graphite.

TABLE I.

ABSORPTION OF THERMAL NEUTRONS (a = absorption coefficient × 10^{-24}).

Capture.	Element.	*a*.
LOW - - - -	Deuterium	0.0006
	Beryllium	0.0085
	Carbon	0.0048
MEDIUM - - -	Magnesium	0.6
	Lead	0.17
	Aluminium	0.24
	Iron	2.5
HIGH - - - -	Silver	57
	Lithium	65
	Gold	95
	Boron	700
	Cadmium	2,500

Taken from "Nuclear Reactors" by Sir John Cockroft,
Pelican Book A 224, London, 1950.)

Resonance Capture.—The nature of the moderator is, however, only *one* important factor in the design of an atomic pile; another of equal importance is the *spacing* of the moderator units relative to the uranium slugs.

It has already been pointed out that the probability of a neutron causing fission in U–235, or becoming captured by U–238, is greatly influenced by the neutron velocity. Thus, if the neutrons have been slowed down to "thermal" level, the ratio of fissions in U–235 to capture in U–238 favours fission; if the neutrons move much faster than "thermal" neutrons, it favours capture. A complicating factor is, however, the fact that there exist certain ranges of neutron speeds at which capture in U–238 becomes so large that the reproduction factor cannot normally be maintained at, or above, unity. These ranges are termed "resonance bands," and the capture of neutrons moving with velocities lying in these bands is referred to as "resonance capture."

If the reaction is to be maintained, resonance capture must therefore be reduced to a minimum by slowing the neutrons so rapidly that they spend only a small fraction of their time at the dangerous speeds. This is now done by arranging the uranium slugs and moderators units in a carefully planned **lattice structure.** Thus, when the neutrons reach energy regions at which they would be strongly absorbed by resonance capture, they will have a good chance of making another collision with the moderator atoms before reaching the uranium.

It should, however, be pointed out that whilst the lattice structure can successfully reduce the resonance trap, it becomes a disadvantage when the neutrons have reached "thermal" levels. At that stage, there is the obvious danger that they will become captured by the moderator before reaching the uranium. Very careful attention must therefore be given to the size of the moderator units.

Neutron Reproduction in Atomic Piles.—In order that a nuclear reactor shall maintain a controlled chain-reaction, the number of "effective" neutrons, *i.e.*, neutrons available for fission of U-235 or plutonium, must be regulated at a level at which the **reproduction factor** (k)—which characterises the relative increase in neutron population in successive generations—is equal to, or greater than, unity. This does not, of course, present a problem in theory; for, since each fission of U-235 is accompanied by the emission of two new neutrons a divergent chain-reaction (with $k=2$) is theoretically a *consequence* of fission (see Fig. 1*a*). In practice, however, it appears that k can only with considerable difficulty be prevented from falling below unity.

In general, there are four ways in which neutrons in any one generation may "die"; they may be captured by U–238 without fission; they may be absorbed by the moderator (or by other materials, such as coolant and fission by-products, also present in the reactor system); they may escape from the reactor by leakage across the surface; or they may cause fission in another U–235 nucleus. In principle, therefore, a chain-reaction is only possible if not more than 50 per cent. of the neutrons generated by the fourth process are dissipated by the first three. If more than this proportion *are* lost without fission, k becomes smaller than 1, each neutron will only produce

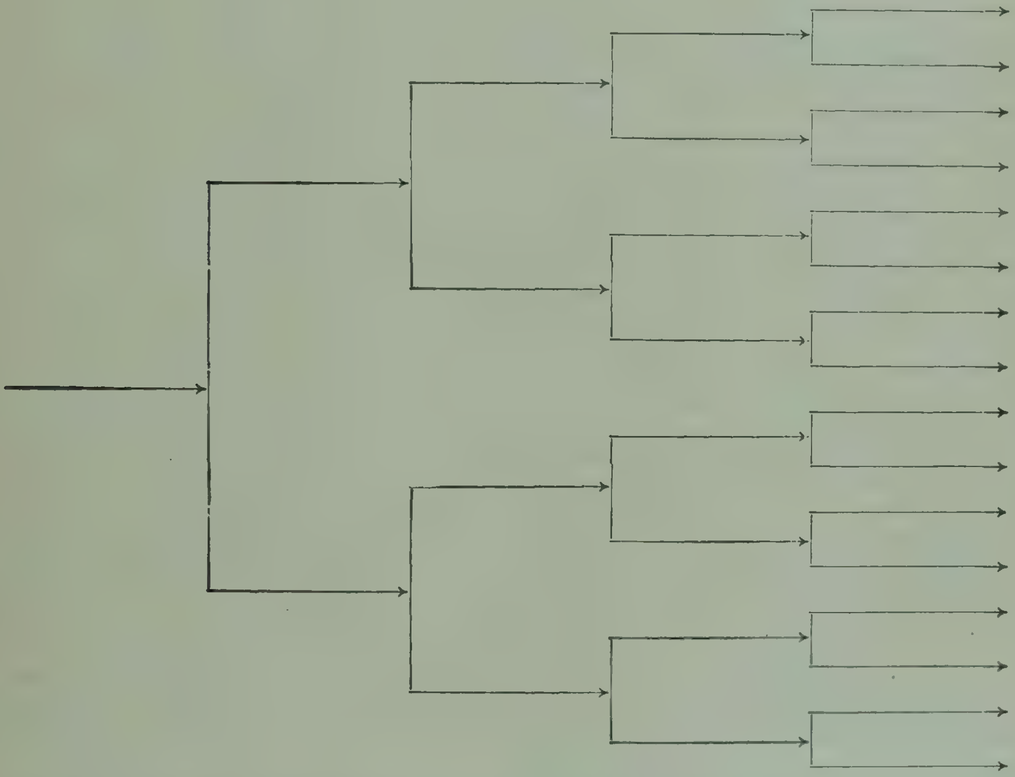


FIG. 1*a*.—Divergent chain-reaction with $k=2$. (Shown up to 5th generation. Neutron population is doubled in each generation.)

$$1+k+k^2+k^3+\ldots=1/(1-k) \text{ further neutrons,}$$

and the reaction will tend to run down (even though additional neutrons—derived from stray cosmic rays and the *spontaneous* disintegration of uranium—may sustain it for a longer period than would be expected from the value of k).

In uranium-graphite piles, in which neutron capture by the moderator alone will normally account for a reduction in the value of k to nearly unity, efforts must therefore be made to minimise the rate of neutron leakage from the system as far as possible. This can be done by increasing the volume surface ratio of the reactor to beyond a certain value, *i.e.*, by making the reacting system larger than a certain **critical size,** and by surrounding it with a **reflector shield** that will return a substantial proportion of escaping neutrons to the reactor. The linear dimensions of the critical size are approximately given by the expression

$$S = D/\sqrt{(k^* - 1)}$$

where D is the distance travelled by a neutron between "birth" and "death," and k^* the reproduction factor of an infinite system, but it will be evident that the actual critical size required for a given neutron leakage will be much smaller with than without a reflector.

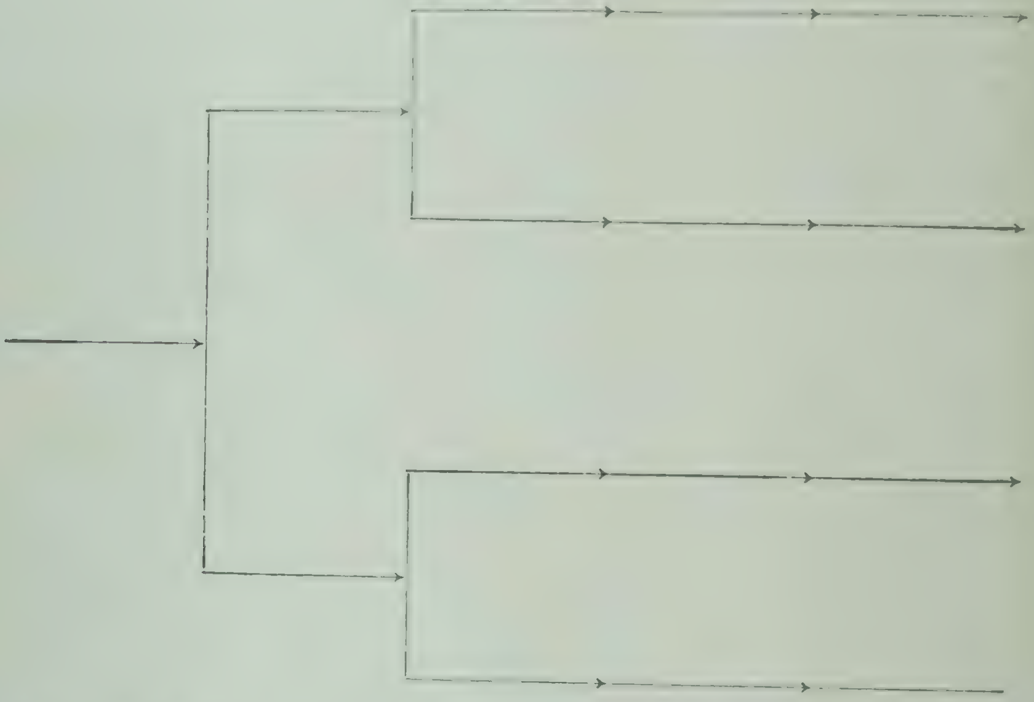


FIG. 1*b*.—Balanced (or Controlled) chain-reaction with $k = 1$ after third generation.

Even with these precautions there remains a very wide margin between theoretical and practical reproduction factors. For example, with a graphite system, k^* cannot exceed 1.07, and in a uranium-deuterium oxide reactor it cannot be larger than 1.15 (Cockroft, 1950). Values of k (*i.e.*, values of the reproduction factor in the corresponding **finite** reactors) will consequently be still smaller.

It should, however, be noted that a controlled reaction is only possible if k is only *slightly* greater than unity. As k increases, the number of neutrons and fissions will begin to grow exponentially with time, following a general law of the type

$$N = N_0 . e^{(k-1)T/t^*}$$

where T is the time in seconds and t^* the lifetime of one generation of neutrons (*c.* 10^{-8} seconds). If, therefore, k were to exceed unity by 0.1 per cent., the time constant of the reaction (*i.e.*, the doubling time) would be of the order of 10^{-5} seconds, and the system would be extremely difficult to control. (For example, it can readily be demonstrated that in order to bring the doubling time to a value of, say, 10 seconds, $k - 1$ would have to be adjusted to within 10^{-9}; this would be virtually impossible, since expansions due to slight temperature changes will alter the value of the reproduction factor by much greater amounts.) In practice, a margin for adjustment is created by the fact that a small proportion of neutrons produced by fission (about 1 per cent.) may be *delayed* by as much as a minute.[1] The average reproduction time is thereby increased and adjustment of the neutron intensity made considerably less sensitive to the value of k. Consider, for example, the case in which k exceeds unity by *less* than 0.01; the "prompt" neutrons here have a reproduction factor of less than unity, and cannot, by themselves, cause a divergent chain-reaction, and since

$$T \simeq 0.7 \frac{(1 - k_p)}{(1 - k)} t$$

where k = reproduction factor due to "prompt" neutrons alone, k = overall reproduction factor, T = doubling time and t = average time between fission and the emission of delayed neutrons (about 10 seconds), it follows that if $k = 1.005$, $k_p = 0.995$, then T = 7 seconds. In other words, the *nuclear reaction will remain balanced if* k *is adjusted to a value lying within the range* 1.000–1.005. If $(k - 1)$ is greater than about 0.005, a divergent chain-reaction results, and the doubling time will decrease progressively more rapidly as the excess of k over unity increases. This principle has been used in the construction of the "atomic" bomb (though, in this case, the fuel is either the highly fissionable U–235 or Plutonium).

Health Hazards in Atomic Energy Research.—Biological ill-effects due to prolonged exposure to radium and other radioactive substances have been known for some time. For example, during the first world war, workers engaged upon the manufacture of luminescent instrument dials, using radium paints, began to develop bone cancer as a result of frequently licking their brushes. Similarly, miners working in the uranium mines at Joachimsthal (in Czechoslovakia) were found to be unusually liable to cancer of the lungs. Modern atomic research work has therefore entailed a detailed study of these effects and of the precautionary measures that must be taken.

In general, it appears that radioactive radiations (*cf.* Section LXXXV) as well as neutrons produce their effects by ionisation and consequent disruption of molecules in the tissues. Thus, genes and chromosomes may be split (with the appearance of mutations); water (an essential constituent of living cells) is ionised to H^+ and OH^- and can then deactivate enzymes; and cell proteins may be split. Dividing cells are found to be the most sensitive to radiations.

There is, however, some uncertainty as to limiting doses to which tissues may be exposed without ill-effects. Experiments with the fruit-fly Drysophila, and later with rats and rabbits, indicate that radiation effects depend not only upon the dose and the extent of tissue exposed to it, but also upon *type* of the tissue. For example, whilst a dose of 500 roentgen units (see below) is sufficient to kill a human being if applied to his whole body, twice this dose, if limited to the skin of his forearm, will do little more than produce a local irritation. In the same way, the fatal dose for a mouse is larger than that for a guinea-pig, but smaller than that for a rabbit. There is, moreover, considerable evidence that the lethal dose may even vary among members of a single *species*; thus, whilst 500 roentgen units were in one instance found to kill about 50 per cent. of a group of mice, it only induced varying degrees of radiation sickness and anæmia in the remainder. Biological research into radiation effects must therefore generally be conducted on large populations and the results expressed statistically.

At present, the only *certain* knowledge relates to the tolerance dose that a man can receive on his whole body without ill-effects. This dose is of the order of 0.5 roentgen unit per day.

The roentgen unit (r) itself is defined as that amount of radiation which will produce enough ionisation in 1 c.c. of air (at N.T.P.) to amount to one electrostatic unit of electric charge. Since a single electron carries a charge of 4.77×10^{-10}

---

[1] Delayed neutron emission is due to the fact that some fission products are transformed by beta-particle emission into nuclei which in turn emit further neutrons. The delay is thus due to the time required for beta-transformation which precedes the "birth" of these neutrons.

electrostatic units, 1r is equivalent to about 2×10^9 electrons per c.c. It must, however, be noted that the biological efficiency of a radiation will depend as much upon its *composition* as upon its quantity.

An *overdose* of radiation manifests itself first in a reduction of the number of white blood cells in the blood stream (and in subsequent progressive anaemia), and secondly (if the overdose is large) in radiation sickness. This has been studied in some detail among the survivors of the atom bomb explosions at Hiroshima and Nagasaki. Those who survived the actual explosion but were near enough to receive a substantial overdose, either died suddenly within about forty-eight hours, or developed sickness, fever, and anæmia. Loss of hair was also a frequent symptom, and a number of patients were subject to repeated hæmorrhages, apparently due to inability of the blood to clot. In many instances it proved possible to cure radiation sickness by blood transfusions and treatment with such anti-bacterial substances as penicillin, but there is some evidence that even the cured subjects may give rise to mutations in later generations. The extent and frequency of these mutations is at present still the subject of investigations.

Protection against Radiation.—Whilst acute radiation sickness is unlikely to occur in peace-time because of the control that can be kept on nuclear reactors, elaborate safety precautions are necessary to shield workers from small, but steady, overdoses over a long period. These precautions fall into two types.

The more important is the effective screening of reactors by concrete, or, in certain cases, by lead. The efficiency of such a screen is roughly proportional to its density, and if concrete is used, the screen must be about four times as thick as a lead shield. The absolute thickness of the screen does, however, depend upon the power generated in the reactor. For example, in order to shield a pile generating the heat equivalent of one watt, the concrete screen must be about one foot thick. Each additional foot will then reduce the radiation intensity by a factor of 10.

The second group of precautions consists of so-called "monitoring" devices, *i.e.*, of instruments capable of registering radiation intensity accurately. With these, a check is maintained on the "hotness" of laboratory benches and working areas as well as on personnel. For example, monitors installed at exits can scan individuals passing through and register radio-active material accidentally retained on boots, under finger nails and in the clothing itself.

For a fuller account of radiation effects and precautions, reference should be made to "The Science and Engineering of Nuclear Power," Vol. II, Chapter 16.

Future Development of Atomic Energy.—At the present time, it is generally agreed that production of controlled atomic energy will be more difficult than had originally been supposed, and that its future cannot be predicted with any degree of certainty until more efficient experimental power units have been built and operated for a number of years. Immediate work is, therefore, likely to be directed towards new designs of piles—particularly of piles capable of generating power at higher temperatures—and towards the development of "breeder" units which can breed secondary fuel (*i.e.*, plutonium) as fast, or faster, than they "burn" U-235. In view of the technical difficulties which these objectives involve, this stage is likely to take a very considerable time.

Some attention will also have to be given to the development of economical methods of extracting uranium from low grade ores. Although uranium is not a scarce element (it is about twenty times as abundant as silver), it is widely disseminated, and deposits containing more than about 1 per cent. of uranium are, in general, small. Large scale production of atomic power may therefore be forced to rely on relatively poor starting material.

A further difficulty relates to the disposal of radioactive waste materials produced in atomic power piles. Whilst health hazards connected with the normal operation of such piles can be reduced (or eliminated) by heavy, though costly, shielding, disposal of radioactive waste by present methods (*e.g.*, dumping in oceans) is bound to increase considerably the amount of radioactive substances dispersed over the planet as a whole, and must sooner or later reach danger level. Alternative methods must consequently be sought, but this will undoubtedly constitute a very formidable task as radioactive phenomena cannot be affected by known chemical or physical techniques. The dumping of wastes in the Antartic has been suggested, but this scheme appears a little fanciful and does not, in any case, constitute a real solution of the problem (even if the additional transport costs can be borne by the economies of the piles).

Finally, there is reason to believe that increasing attention will also be given to the possibility of releasing energy from light elements by a *synthesis* process. In a British Association Report of 1920, Eddington pointed out that the sun's radiation could be maintained at its present level for about 1,000 million years by the conversion of 10 per cent. of its hydrogen into helium. The possibility of this conversion was proved experimentally by Bethe, Gamow *et al.* between 1932 and 1939, and it has been suggested that the conversion involves a reaction chain in which carbon-12 is transformed into carbon–13 and finally nitrogen–15, which is then broken down to carbon–12 and helium. This cycle, however, requires temperatures of the order of 20 million degrees, and future work is therefore likely to centre around other (simpler) cycles that have more recently become known: for example, if deuterium is formed by the interaction of two hydrogen nuclei, a reaction between two deuterium nuclei will result in the formation of tritium, and this can in turn interact with deuterium to form helium. It is believed that this cycle, which can operate at much lower temperatures, does, in fact, take place in certain stars, and it is known that it will release substantially more energy than the disintegration of uranium.

As matters stand, however, most work on atomic energy is still highly speculative, and it is even doubtful whether it will ever be possible to design power units that are sufficiently small to be carried in ships.

The new atomic power station to be constructed at Calder Hall, which is said to be capable of producing "sufficient power for a small town" will cost between £1,000,000 and £2,000,000 and will tkae approximately eighteen months to build.

Orthodox generators driven by steam turbines will be used. The atomic pile will produce the heat to generate the steam to drive the turbines.

A new type of atomic reactor will use natural uranium as the fuel, probably enriched by a small amount of the much more active Uranium 235, which is now being produced in satisfactory quantities at one of the big northern "atom factories."

The whole atomic reactor will be housed in a metal shell, filled with inert gas. This gas will be pumped through the uranium, carrying away the heat generated by the atomic reaction.

The gas, now at very high temperature, will be recycled through a heat exchanger, and the heat will be used to raise steam for the turbines.

NOTES

NOTES

INDEX

SUBJECT INDEX

A

Aalborg kiln, 111, 112
Abbé ball mill, 23, 93
Abrasive grinding wheels, 434
— mill-stones, 434
— powders, 437, 438
— stones, 434
— wheels, 434
Abrasives, 434
— cloths, 439
— for dentifrices, 439
— papers, 439
Abrastol, 3
Accelerators, for plaster, 124
Acetic acid, disinfecting properties, 3
Acetylene, 427
Achromatic glass, 290
Acid, benzoic, 3
— hydrocyanic—see *Hydrocyanic acid*
— nitric—see *Nitric acid*
— salicylic, 3
— sodium sulphate, disinfecting properties of, 12
Acids, disinfecting properties of, 12
— germicidal value of, 10–11
Acriflavine, 4
Actinolite asbestos, 313
Actol, 15
Adobe clay, 154
Aerosporin, 16*a*
Aeschynite, 291
Agate pestles and mortars, 415
Agyrol, 15
A.L. 63, 20*b*
Alabaster glass, 297
Alby carbide furnace, 427
Alexandrite, 63
Alkalis—see under *Sodium hydroxide, Sodium carbonate, Potassium hydroxide, Potassium carbonate, Lime, etc.*
— action on glass, 268
— estimation of, 128
— presence in fire clays, 252
— removal from water, 61
Alluvial clay, 144
Almandine, 63
Altmann's process, 9
Alum, 49, 54, 55, 56, 57
Alum, action on plaster, 124
— ammonium iron, 56
— burnt, 56
— cake, 54
— iron in, 57
— potassium, 55, 56
— — chrome, 56
— properties of, 51, 52
— replacement by aluminium sulphate, 49, 56
— shales, 55
— sodium, 56
— stone, 55
— uses, 51, 52, 273, 308
— waterproofing by, 118, 119
Alumina, 49–52
— bricks of, 249
— estimation of, 128
— fused, 52
— manufacture of, 49–51
— packing for acid towers, 52
Alumina cements — see *High alumina cements*
Aluminate, sodium, 50, 51, 52, 56
— calcium, 109, 110, 111
Aluminium, 49, 51, 332
— acetate, 56
— action on charcoal, 68
— action on iron oxide, 68
— action on lead sulphide, 67
— action on metallic oxides, 68
— action on metallic sulphides, 67, 68, 69
— alloys of, 325, 327
— and chrome ores, reduction of, 431
— chloride, 15, 56
— compounds, industry of, 49–57
— fluoride, 52
— hydroxide, 49, 50, 51, 52
— oxide—see *Alumina*
— powder as deoxidant, 76*a*
— powdered, world production of, 76*a*
— reduction of metals by, 69
— salts, disinfecting properties of, 15
— — uses of, 56, 57
— silicates, 60, 116
— silicofluorides, 127
— soaps, 57
— sterilising effect of, 15
— sulphate, 52–57
— — iron free, 51, 52, 53

Aluminium sulphate, manufacture of, 52–54
— — properties of, 54
— — replacement of alum by, 56
— — world production of, 58
Alumino-silicates, 60, 116, 139, 142
Alumino-silicic acids, 140–142, 150, 183
Aluminothermics, 67–76
Aluminol, 3
Alundum, 421, 437
Alunite, 55
Amber mica, 322
American natural cements, 86
Amethysts, 63
Ammonal, 76*a*
Ammonia, "free and saline," 8
Ammonium alum, 56
— carbonate, conversion into potassium carbonate, 61
— chlorate, 61
— iron alum, 56
— sulphate, from nitrolim, 411
— — statistics of, 47
— — use as manure, 36
— superphosphate, 42
Amosite, 314
Amphibole asbestos, 313
Amphoteric oxide, 259
Analcite, 59
Anastigmatic glass, 290
Anatase, 347
Andeer's lotion, 2
Annealing glass, 287
Anthophyllite, 313, 314
— asbestos, 282
Antibacterial drugs, 16
Antibiotics, 16
Antiformin, 6
Antimalarials, 16
Antiseptic power, 1
Antiseptics, 1–16
— testing of, 1
Aphides, 20*b*
Aquamarine, 63
Architectural faience, 167
Archless kiln, 228
Argentamine, 15
Argonine, 15
Armoured concrete, 118
Arsenic acid, use in glass making, 272
— compounds, 20*a*
— disinfecting properties of, 12
— oxide, disinfecting properties of, 12, 20*a*
Arsenical dips, 20*a*
Arsenious oxide, 20*a*
— — in glass, 272
Arsenite of soda, disinfecting properties of, 12, 20*a*
Art enamels, 309
Artificial gems, 63
— guanos, 42
— manures, 21–47
Artificial marble, 140
— stone, 139
— teeth, 191
— zeolite industry, 59–61
Asbestos, 313–319
— actinolite, 313
— amphibole, 313
— anthophyllite, 313
— blue, 314
— cement, 318
— chrysotile, 314
— crocodolite, 314
— grading and classification, 319
— packing materials, 317
— paper and millboard, 318
— preparation of, 315
— resin-bonded products, 318
— serpentine, 314
— textiles, 317
— thermal insulating compositions, 318
— uses of, 317
— world production of, 315
Asbestosis, 319
— bodies, 319
Asch's theory of clays, 151
— — of glass, 255
Atomic absorption of thermal neutrons, 458
— critical size, 460
— divergent chain-reaction, 459
— energy, development of, 462
— finite reactors, 460
— health hazards in atomic energy research, 461
— neuclear reactors, 458
— neutron moderators, 457
— — reproduction in atomic piles, 458
— "piles," 456
— power, 455
— protection against radiation, 462
— reproduction factor, 459
— resonance capture, 458
Aventurine, 174
— glass, 295
Avery compression testing machine, 132
Avery's automatic hopper weigher, 114
Auromycin, 16*a*
Autunite, 387

B

Bacillus aerosporus, 16*a*
Bacterial manures, 39
Balas ruby, 63
Ball and tube mills, capacity of, 94
— clays, 154, 164, 170, 176
— mills, 24–26, 89, 94, 95, 414
Barium carbide in glass, 248, 253
oxide in enamels, 277

Barium oxide, influence on glass, 248
— peroxide, action of aluminium on, 68
— — use in glass-making, 248, 249
Barrow, brick, 207
Baryta, use as glaze, 162
— use in glass, 248, 253
Basic bricks, 249
— cinder, 32
— phosphate, 32
— slag, 32–33
— — statistics, 47
— superphosphate, 31
Basins, 187
Batchelor kilns, 110
Bauxite, 39, 55
— bricks of, 233
— manufacture of aluminium sulphate from, 52, 53
— world production of, 57
Bead glass, 252
Belite, 136
"Bengal Ruby" mica, 324
"Bengal White" mica, 324
"Bengal Yellow" mica, 324
Benzene, cement resisting, 148
— compositions insoluble in, 148
— tight joints, 148
Benzoates, disinfecting properties of, 5
Benzoic acid, disinfecting properties of, 3
Benzol—see *Benzene*
Benzoyl sulphonic imide, 4
Beryl, 63
Beryllium aluminium silicate, 63
Beta-naphthol, disinfecting properties of, 2
— — sulphonates, disinfecting properties of, 3
Beth dust collector, 103, 114
Beton, 125
Biotite, 321, 322
Biscuit ware, 186
Bitten, 125
Black glass, 296
— overglaze, 200
Blacklead, 441
Blacks, in pottery, 175
Blake stonebreaker, 92
Blake-Denison automatic weigher, 114
Blake-Marsden crusher, 92
Blast furnace slag, 83, 119
Bleaching powder, disinfecting properties of, 6
Bleriot lamp, 334
Blisters in glass, 260
Blocks, flooring, 243
— partition, 243
— paving, 211
Blood meal, 39
Blowing of cement, 115
Blown glass, 279
Blue asbestos, 314
— clays, 169
Blue glass, 295
— lias lime, analysis of, 81
Blueing of clays, 170, 174
Blunger, 176
Body of earthenware, 175–180
— of porcelain, 196
— of pottery, 168
Bohemian glass, 264
Boiling test for cement, 133
Boll weevil, 20*a*
— cotton, 20*b*
Bombs, incendiary, 71, 72
Bone ash, 194, 443
— charcoal, 443
— china, 195, 197
— crushing of, 33
— dissolved, 32
— earth, 443
— manures, 32, 33
— meal, 32, 33
— porcelain, 163
— statistics, 47
— steamed, 33
— use as manure, 32, 33
Boot blackings, 442
Boracic acid, 172
— — in glass, 271
Borate glasses, 220, 271
Borax, 253, 271, 275
— action on plaster of Paris, 124
— disinfecting properties of, 10
Bordeaux mixture, 17
Boric acid, disinfecting properties of, 10
— anhydride in glass, 275
— — in enamels, 308
Boro-flint glass, 242, 249, 264, 271
Boron alloys, 70
Borophosphate glasses, 272
Borosilicate glass, 268
— glasses, 273, 287
Bottle glass, 262, 274
— — brown, 275
— — champagne, 264
— — green, 275
— green glass, 291
— kiln, 109
— lutes, 148
— machines, 279
Boulder clay, 155
Bowl making machines, 182
Bradley-Craven brick machine, 225
— three-roll mill, 26, 96
"Break-point," 8
Brick clays, 155
— earths, 155
Bricks, 213–237
— alumina, 249
— baked, 228
— barrow for, 226
— basic, 249
— bauxite, 249

Bricks, buff, 217
— building, 213, 250
— burning of, 228
— chromite, 249
— common, 213
— crushing strength of, 214
— drying of, 226
— engineering, 214
— facing, 213
— fireclay, 247
— fire-proof, 245
— furnace, 245
— glazed, 167, 214
— improvements in manufacture, 236
— iron in, 216
— kilns for, 228–236
— lime in, 216
— literature, 213
— machines for, 223, 225
— magnesia, 249
— magnesium aluminate, 249
— metallurgical, 248
— neutral, 249
— open air driers, 227
— plastic, plant for, 223
— raw materials for, 215
— red, 216
— refractory, 214
— requirements of, 214
— resistance of, in furnaces, 248
— sand-lime, 141, 215, 239
— semi-dry process, 224–226
— silica, 248
— steel furnace, 249
— stiff-plastic process, 222–224
— stock, 213
— testing, 212
— tunnel driers for, 224–228
— vitrified, 228
— weathering of, 250
— white, 217
— zirconia, 249
Broadbent stone-breaker, 92
Bromidine, 10
Bromine, disinfectant properties, 10
Brookite, 347
Broughton mixer, 116
Brown glass, 296
— overglaze, 199
Brunswick black, 441
Burnett's fluid, 16
Brühler glass bottle machines, 282
Bührer continuous kilns, 232
Buff bricks, 217
— burning clays, 159, 170
Buffing, 441
Building bricks, 213, 250
— lime, 81
Bungs, 187
Butt-welding, thermite, 71
Buxton lime, analysis of, 81

C

Cairngorm, 63
Calcareous cement industry, 77–136
Calcium aluminates, 116–119, 135
Calcium arsenate, 20*a*
— arsenite, 20*a*
— carbide, 425
— — residues, manurial value of, 41
— carbonate, burning to lime, 78–81
— — in glass, 269
— — use as manure, 41
— chloride, removal from water, 60
— — analysis of, 38
— — manurial value of, 37
— cyanamide, 427
— fluoride, 51
— — in glass, 269
— — in phosphates, 28
— hydride, 68
— — action of aluminium on, 69
— hypochlorite, disinfecting properties of, 6–9
— metallic production of, by reduction with aluminium, 76*a*
— nitrate, manurial value of, 36–37
— permutite, 60
— phosphate, 21, 23, 28
— phosphide, 449
— salts, removal from water, 60
— — use as manure, 41
— silicate, 84, 260
— — stone, 130
Callow, 217
Cameos, 288
Canadian asbestos, 314
— mica, 324
Carbide, calcium, 427 *et seq.*; see also *Calcium carbide*
Carbo-corundum, 437
Carbolic acid, 20
— — coefficient, 1
— — dips, 20*a*
Carbon dioxide, 11
— filaments, 353–355, 373
— — efficiency of, 366
— — lamps, 351–355
— tetrachloride, 4
Carbonaceous zeolites, 61
Carborundum, 414–419, 437
— decomposition of, 417
— furnaces for, 414–416
— literature, 413
— manufacture, 414–419
— properties of, 417
— statistics, 417
— temperature of formation, 415
— uses of, 417
"Carborundum firesand," 416
Carmine overglaze, 199
Carnallite, 127

Carnallite, use as manure, 41
Carnotite, 387, 393
Carter's disintegrator, 26–27
Carthamus tinctoris, 439
Cassius purple, colouring pottery with, 175
Casting earthenware, 182
— porcelain, 197
— sanitary ware, 209
Castor oil meals, use as manure, 38
Catalase, 5
Catechol, disinfecting properties of, 2
Caterpillars, 20*a*
Ceiling plaster, 121
Celite, 137
Cement, acceleration of set, 127
— acid resisting, 135–137
— American natural, 86
— analysis of, 127–129
— Avery testing machine, 130
— — compression testing machine, 132
— blowing of, 115
— boiling test, 133
— burning to clinker, 100 *et seq.*
— chemical analysis of, 127
— classification, 77, 78
— clays, 145
— clinker, storing of, 111
— constancy of volume and soundness, 133
— constituents of, 116
— crushing strength of, 131
— dental, 148
— dry process for, 99
— fineness of, 129
— flour, 99
— French quick-setting, 86
— Grappier, 82
— grinding, 84, 92–99, 113
— industry of, 77–137
— iron ore, 120
— iron Portland, 85
— Keene's, 125
— kilns for, 100 *et seq.*
— Louisville, 86
— Mack's, 125
— magnesium oxychloride, 137
— marble, 140
— medina, 85
— microscopic examination, 135
— mixing, 84, 88
— mortar, 125; waterproofing of, 126
— natural, 85–87
— — Portland cement, 86
— nature of, 77
— packing, 113
— Parker's, 85
— parian, 125
— Passow's slag, 84
— physical and mechanical tests, 129
— plaster, 125
— Portland, 128; see *Portland cement*
— ponilly, 86
Cement, puzzuolanic, 83, 85
— rock, 86
— Roman, 85
— rosendale Portland, 86, 87
— sand, 113
— Scott's selenitic, 83
— semi-wet, 89
— setting of, 117
— setting time of, 131
— sidero, 119
— slag, 83–85
— Snelus, 85
— Sorel, 137 *et seq.*
— soundness of, 124
— specific gravity determination, 129
— storing, 113
— super, 120
— tensile strength of, 129
— test piece, 130
— Vassy, 86
— vicat needle, 132
— wet process for, 88 *et seq.*
— white Portland, 120
Cements, calcareous, 77 *et seq.*
— and sulphuric acid, 135
— hydration of, 117
— slurry making process, 90
— vertical slurry mixing and tanks, 91
— see also *Sodium silicate*
Ceramic industry, 161–237
Ceria, separation of, 343
Cerite, 342
Cerium, 342
— estimation of, 346
— in industry, 343
— metallic, 343
Chabazite, 59
Chalk, 78, 438
— in clay, 214
— use as abrasive, 438
Champlévé enamel, 309
Champagne bottle glass, 264
Chaux de Theil, 82
Chemical apparatus fabricated in fused quartz, 301
Chemical stoneware, 207–212
China, bone, 197
— English, 197
— clays, 155, 170, 176, 193
— — aluminium sulphate from, 54
— stone, 194
— ware, 163
Chinese porcelain, 196
Chinosol, germicidal value of, 3
Chloramines, 8
Chlordane, 20*c*
Chloride of lime—see *Bleaching powder*
Chlorination of water, break-point, 7
Chlorine, disinfecting properties of, 3, 8–9
— free, 8
— test for free, 9

Chlorine water, germicidal value, 3
Chloroform, 6
Chloromycetin, 16*a*
— arsenite, 20*a*
— arsenate, 20*a*
Chloros, 9
Chrome alum, 56
— aventurine glass, 295
Chromic acid, disinfecting properties of, 12
— oxide, colouring with, 174
Chromite bricks, 233
Chromium alloys, 70
— colouring glass by, 295
— metallic, 68–69
— steel, 69
Chrysoberyl, 63
Chrysotile, 314
— asbestos, 314 *et seq.*
— properties of, 316
Ciment grapier, 82
Cisterns, cements for, 147
Citric acid, 5
Clark's mill, 89, 90
Claude process, 84, 85, 89, 113
Clay, 149–160; see also *Kaolin and China clay*
— absorption of dyes by, 150
— action of heat on, 150
— adobe, 154
— alluvial, 154
— alum for, 54, 55
— analysis of, 159, 160
— ball, 154, 169, 170, 176
— blue, 169
— boulder, 155
— brick, 155, 215
— buff-burning, 159, 170
— cement, 155
— chalk in, 216
— chemical constitution of, 149–152
— China, 54, 155, 170, 176, 193
— connection between composition and refractory properties, 245, 246
— consistency of, 178
— crucible, 156
— earthenware, 169
— effect of heat on, 170
— electrical osmose of, 153
— expression of, 222
— fire, 156
— flux for, 153
— fusing point of, 247
— impurities in, 153
— jolleying, 181
— literature, 149
— melting point of, 247
— moulding, 180, 220
— pipe, 157
— plasticity of, 152, 179
— puddling of, 157
— purification of, 153
Clay, quarrying of, 217
— red-burning, 157, 170
— refractory, 157, 247
— resistance to heat, 246
— sagger, 157
— shaping of, 179–184
— shrinkage of, 153, 154
— softening points of, 246
— stiff-plastic process, 222
— surface, 158
— tempering of, 219
— tender, 158
— throwing, 180
— turning, 180
— varieties of, 154–159
— vitrifiable, 159
— washing of, 217
— wire-cut process, 222
— yellow, 159
Cloisonné enamel, 309
Coal tar disinfecting liquids, 4
Cobalt, colouring glass by, 295
— oxide, 199
— — blueing with, 170, 174
— — colouring with, 174, 295
Coffee-mill grinding machine, 86, 92
Colloidal theory of clays, 142, 143
Colour mill, 181
Coloured glass, 294
— stones based on corundum, 65
Colours, earthenware, 173–175
— glazing, 201
— porcelain, 201
Columbite, 361
Columbium, 365
Common bricks, 213 *et seq.*
Complete exchange zeolites, 61
Compo, 98
Composite glaze, 205
Compound mills, 97, 98
— tube mill, 98, 99
Concrete, 117, 118, 129
— armoured, 118
— refractory, 134
— reinforced, 118
— waterproofing of, 118, 119
Condy's fluid, 7
Continuous kilns, 232
Cooker, continuous, 35
Coolers, cement, 102, 103
— Mosser, 103
— shaking, 103
— Smidth, 102
Copper acetoarsenite, 20*a*
— alloys, 70
— disinfecting properties of, 14
— ruby glass, 291
— salts, antiseptic properties of, 14, 17
— sulphate, germicidal value of, 3, 14, 17
— — use as insecticide, 17
Coprolites, 21, 23

Cornish stone, 167, 171, 176, 194
Corrosive sublimate, 18
Corubin, 437
Corundum, 52, 63, 64, 437
— artificial, 65
— wheels, 434
Crackers, 86
Crackled ware, 199
Crazing, 199
Cresylic acid, germicidal value of, 3
— — uses as disinfectant, 4
Crocidolite, 314
— asbestos, 314
Crocus martis, 174
Crown glass, 274 *et seq.*
Crucible clays, 156
Crucibles, manufacture of, 248
Crushed steel, 438
— — use as abrasive, 438
Crusher, Blake-Marsden, 92
— gyratory, 92, 93
— rotary, 86, 92
— Wheeling, forced feed, 92
Crushing machinery, 24, 92, 93
— rolls, 414
— strength of cement, 122
— tools, 414
Cryolite, 51, 55, 175
— in enamels, 307
— in glass making, 273, 298
Crystalline glazes, 199
Crystolon, 437
Culinary stoneware, 207 *et seq.*
Cullet, 273
Cultured pearls, 65
Cummer rotary calciner, 115
Cup making machine, 182
Cupric oxide, colouring with, 174
Cuprous chloride, disinfecting properties of, 14
Cyanamide, 427
— calcium, 37, 38; see also under *Calcium cyanamide*
— literature, 413
Cyanide, iodine, 6
— potassium—see also *Potassium cyanide*
— sodium—see *Sodium cyanide*
Cymophane, 63

D

2.4-D, 19
D.D.T., 20*b*
Davidsen tube mill, 96
Decolorants for glass, 273
Decoration of earthenware, 189
Delft ware, 167
Della ware, 167
Demantoid, 63
Dens, superphosphate, 30, 31
Dental cements, 148
Deplinne and Donop's kiln, 79
Derris elliptica, 20*b*
— powder, 20*b*
Dettol, 4
Deuterium, 457
Devitrification of glass, 259
Diamantin, 421
Diamond wheels, 436
Diamonds, 63, 64, 437
— artificial, 64
— imitation, 65, 265
— powder of, 437
— use as abrasive, 437
Diastase, 7
2.4-Dichlorophenoxy-acetic acid, 19
Diethyl paranitro-phenyl-thiophosphate, 19
Dietzsch kiln, 110
Dioxogen, 7
Diphenyl, 19
Dippel's animal oil, 443
Disinfectants, 1–16
— oxidising, 6
— testing of, 1–3
Disintegrators, 26, 27, 93
Dissolved bone compound, 32
— guanos, 42
— raw bones, 32
Dolomite, 270
Dolomitic lime, analyses of, 11, 81
— limestone, 78
Dome kiln, 110
Down-draught kiln, 229
Drain-pipes, 210
Driers, 83, 84
— brick, 212
— rotary, 34, 35, 92
— steam, 34
— tunnel, 89, 100, 227
Driwal, 118
Drops, Rupert, 265
Drying earthenware, 183
— plant for slag, 83, 84
— process for cement, 88, 89
— stoves, 183
Dumesnil kiln, 122
Dung, use as manure, 42, 43
Durax glass, 292
Dymal, 321

E

Earth, brick, 155
— fullers, 156
Earthenware, 161–193
— bodies, 175–179
— calcareous, 167
— classification of, 167
— clays for, 169
— coarse, 167
— constituents of, 168
— decoration of, 189

Earthenware, drying, 183
— engobing, 182
— fine, 167
— furnaces for, 187
— glazed, 167
— glazes for, 188–189
— machines for, 182
— mixing materials for, 176
— overglaze decoration of, 190
— painting of, 189
— printing of, 189
— progress in, 191
— shrinkage of, 184
— siliceous, 168
— underglaze decoration of, 190
Eau de Javel, 9
— — Labarraque, 9
Edge-runners, 88, 89, 107, 218
Eisen Portland cement, 85
Electrical furnace, alundum, 421
— — carbide, 425–426
— — glass, 279
— — graphite, 420
— — phosphorus, 427
— purification of clays, 153
Electric lamp industry, 373
— carbon filaments, 373
— cold cathode tubes, 385
— colloidal tungsten filaments, 378
— drawn wire tungsten filaments, 378
— fluorescent lighting, 385
— gas-filled lamps, 384
— lamp ratings and efficiencies, 384
— metallic filament lamps, 374
— tantalum lamps, 375
— tungsten lamps, 375
— vacuum lamps, 382
Electro-magnetic separation, 178
Electrodes, graphite, 420
— graphitised, 420
Electrolysis, graphite electrodes for, 420
Embossing glass, 288
Emerald, 63
Emery, 52, 437
— cloth, 438
— paper, 438
— wheels, 434
Enamel cements, 148
— glaze, 148
Enamels, 175, 305–311
— art, 310
— colours for, 308, 310
— composition of, 307–310
— continuous firing equipment for, 309
— ground coats for, 305
— painting, 311
— printing of, 311
— varieties of, 305
Enamelling furnaces, production capacities of, 311
Encaustic tiles, 241
English china, 197
— sheet glass, 264
Engobe, 168, 169
Equalised guanos, 42
Estrich gips, 116
Etching glass, 288
Ethylene diamine silver phosphate, 16
Eucalyptol, germicidal value of, 3
Eucalyptus, use as disinfectant, 5
Eutectics, 135
Expansion test for Portland cement, 124
Expression of earthenware, 182

F

Facing bricks, 213
Fæces, use as manure, 42, 43
Fahnejelm's kiln, 80
Faience, 163, 167
Faija test, 124
Farmyard manure, 43
Fats, manufacture from flesh meal, 34
Fawcett's brick machine, 224
Felite, 110–111, 125
Felspar, 171, 194, 201
— use in opaque glass, 296
— weathering of, 59
Fergusonite, 361
Ferric oxide, estimation of, 119
Ferrite, sodium, 50
Ferrites, 109
Ferro-boron, 70
— chlor treatment of water, 8, 9
— molybdenum, 70
— silicon, 422 *et seq.*
— titanium, 70
— vanadium, 70
Ferrous sulphate, disinfecting properties of, 1
Fertilisers and Feeding Stuffs Act, 1926, 47
Fertilisers, availability of nitrogenous, 48
— limits of error, 44
— plant for, 22
— production of, 47
— statistics, 47
Fibrous plaster, 118
Figured plate glass, 286
Filter press, for slips, 178
Finishing earthenware, 182
Fire-bricks, 234, 247, 256; see also *Fir* *clay, bricks, etc.*
— clay, 156, 246
— proof asbestos preparations, 317
— sand, 416
Firing earthenware, 187
Fish, guanos, 34, 36
— manures, 34
— scrap, 34
Fitzgerald carborundum furnace, 415
Fixation of nitrogen—see *Nitrogen, fi* *tion of*

Flare kiln, 79
Fleck's phosphorus process, 444
Flesh meal, 34
Flint, 173, 176
— glass, 274
Flooring asbestos, 317
— blocks, 243
— composition, 128
Flooring plasters, 113, 116
Flowing glass, 200
Fluates, 119
Fluorides, calcium, 51
— disinfecting properties of, 11
Fluorine in enamels, 308
Fluorspar, 175, 296
Fluted sheet glass, 287
Flux for clays, 153
— for earthenware, 170–173
Ford's silicate of lime stone, 130
Formaldehyde, 20*b*
— disinfecting properties. 3, 5, 18
Formalin—see *Formaldehyde*
Formic acid, disinfecting properties, 3, 5
Foucault's sheet-glass machine, 284
Foucault process for glass, 284
Fray-Bentos guano, 34
French polish, 442
Frits, 188, 196
Fritting, 188
Fritz, 172
Frosting glass, 288, 289
Fuels for pottery ovens, 177
Fuller Lehigh mill, 96
Fuller's earth, 146
Fungicides, 17–20
Furnace bricks, 211
— linings, 156, 245–251
Furnaces, Alby carbide, 409–410
— alundum, 406, 407
— carbide, 427
— carborundum, 414–416
— cements for, 146
— earthenware, 185
— electric, 255, 413–432
— ganister linings of, 245
— glass, 279
— improvements in, 191
— silicon, 423
— temperature of, 187
Furniture polishes, 442
"Fused silica," 300

G

Gadolinite, 327, 342
Galena, 173
Gammexane, 20*b*, 20*c*
Ganister, 156, 232
— furnace linings, 245
Gan's zeolites, 59, 60
Garnets, 63, 438
Gas, lighters for, 316, 317
— mantles, manufacture of, 336
— retorts, 231
Gauges, glass for, 265
Gems, 63–65, 292
Gerbel-Strover furnace, 406, 407
Germicidal power, 1
— value, 1, 3
Geyserite, 173
Gibbon kiln, 110
Gilded glass, 297
Gilding, 199
Glass, 253–304
— achromatic, 290
— actinic ray, opaque, 291
— — — transparent, 291
— action of alkalis on, 268
— action of superheated water on, 268
— alabaster, 297
— anastigmatic, 290
— annealing, 262, 287
— — point, 262
— arsenic, 272
— artificial gems, 292
— Asch's theory of, 253 *et seq.*
— atmospheric influence on, 268
— aventurine, 295
— baryta, 279
— Bastie's hardening process, 267
— bead, 278
— bending of, 287
— black, 296
— blisters in, 260
— blown, 277
— blowing, 282
— blue, 297
— Bohemian, 264
— boracic acid in, 271
— boroflint, 264, 271
— borophosphate, 272
— borosilicate, 274, 291
— bottle, 264, 276
— — green, 297
— — machines, 282–284
— brittleness of, 268
— brown, 276, 295
— carboys, 283
— carnegeite in, 260
— casting of, 286
— cements for joining metals to, 148
— chemical, 291
— — composition of, 254 *et seq.*
— — properties of, 268
— chimneys, 292
— chrome aventurine, 296
— classification of, 274
— cold air for quenching, 267
— coloured, 276, 294
— — ions, 258
— compression strength, 266

Glass, continuous filament fibre, 265
— corundum in, 260
— cristobalite in, 260
— crown, 274
— cryolite in, 273
— crystal growth rate, 261
— cutting of, 288
— decay of, 294
— decolorants for, 273
— defects in, 285, 293
— density of, 266
— devitrification of, 259
— devitrite in, 260
— diopside in, 260
— disannealed, 267
— drawn sheet, 283
— effect of alumina on, 259
— elasticity, 266
— electrical insulating, 292
— embossing of, 288
— English sheet, 264
— engraving of, 288
— etching of, 288
— expansion of, 266
— fibre, 265
— flashing of, 294
— flint, 264, 276
— Foucault process, 283
— frosting of, 288
— furnaces for, 279
— fusibility, 259
— geräte, 291
— gilded, 298
— green, 295
— grinding of, 288
— hardened, 267, 287
— hollow ware, 275, 289
— homogeneity of, 266
— impact strength, 266
— industry, commercial importance of, 254
— insulating, 292
— iridescent, 289
— Jena, 264, 269, 271, 276, 291
— laboratory, 264
— large vessels of, 283
— lead, 271
— Libby-Owens machine, 283
— liquidus curve, 259
— literature, 253
— lower annealing temperature, 262
— melting point of, 267
— milk, 51, 297
— miner's lamp, 277
— mixing materials for, 275
— mixture, theory of, 259
— modern views on constitution, 297
— modifier, 259
— mullite in, 260
— nature of, 253
— nephilite in, 260
— network formers, 257, 259
Glass, normal, 254
— opal, 295
— opaque, 274, 292
— — to infra-red rays, 266
— — to ultra-violet rays, 266
— — white, 295
— optical, 290
— — properties of, 266
— paper, 439
— phase diagram, 261
— phase-equilibrium diagram, 259
— phosphate, 277
— photographic, 290
— physical state and viscosity values for, 262
— pink, 295
— planed, 277
— plastic deformation, 268
— plate, 264, 277, 283
— pot-metal colouring of, 293
— pots for, 280
— pressed, 264, 270, 287, 289
— — ware, 289
— properties of, 265
— pseudo-wollastonite in, 260
— quartz in, 260, 299–304
— random network, 257
— raw materials for, 269
— recipes for, 276
— red, 295
— refining, 277
— reinforced, 286
— resistance to atmosphere, 268
— rod, 265
— Sackurs', 291
— Saint Gobin, 264
— sand blast for, 288
— seeds in, 260
— sheet, 278, 283, 284
— silica, 299
— silica-free, 277
— silver stain, 295
— softening point, 262
— specific heat of, 267
— spun, 265
— stained, 293
— staple fibre, 266
— steam boiler gauge, 291
— "stones," 260
— stones in, 285
— strength of, 266, 267
— striæ in, 285
— stringiness of, 285
— table, 264, 277
— tanks, 286
— temperature/viscosity curve for soda lim
262
— tensile strength, 266
— thermal endurance of, 266
— thermometer, 291
— Thuringen, 264, 269
— toughened, 267

Glass, transmitters of infra-red, 259
— transparency of, 266
— tridymite in, 260
— tubing, 265
— tumblers, 283
— typical analysis of, 264
— ultra-violet light transparent, 291
— upper annealing temperature, 262
— uviol, 291
— Venetian, 264, 270, 299
— violet, 295
— viscosity of, 253
— water, 277
— white, 265
— — opaque, 295
— window, 253, 273, 278
— wollastonite in, 260
— working of, 255–262, 280–288
— X-ray bulb, 277
— yellow, 295
— Zschimmer's, 291
Glasses, melting temperatures of, 263
— normal, 254
— properties of, 265
Glassy porcelain, 195
Glaze, 195–198
— composition of, 205
— crystalline, 199
— earthenware, 171, 188–189
— flowing, 200
— lead, 173
— lead-free, 167
— lustre, 202
— sanitary ware, 209
Glazed bricks, 214
— tiles, 242
— porcelain, 199–203
Glazing of grinding wheels, 435
Globe granite, 129
Glost, 186
— firing, 189
Glycozone, 7
Gold, colouring glass with, 297
— — pottery with, 175
— chloride, colouring pottery with, 175
— overglaze, 200
— precipitation of, 61
Goldschmidt's reactions, 67–75
Goreham process for cements, 89
Graf von Schwerin's clay purification process, 153
Graphite, 418
— deflocculated, 420
— electrodes, 420
— literature, 413
— mode of formation, 419
— powder, 420
— properties, 420
— statistics of, 420
— temperature of formation, 419
— uses, 421
Graphitising of electrodes, 420
Grappier cements, 83
Greenfly, 20*c*
Green glass, 297
Greenland, cryolite deposits of, 51
Griffin mill, 95, 96
Grinding and polishing materials, 433
— grade and grain for different classes of work, 436
— hard mineral abrasives, 434
— mild mineral abrasives, 434
— waxy polishes, 434
— wheels, glazing of, 435
Grinding appliances, 434–437
— glass, 288
— machinery, 24–26, 93–98
— materials, 52, 128, 437 *et seq.*
— mills, 434
— plaster, 115, 116
— powders, 437 *et seq.*
— slag, 84
— wet, 88, 89
— wheels, 435
Grindstones, carborundum, 435
Gritstone wheels, 435
Grog, 156, 173, 248
Ground coating for enamels, 308
— mica, 323
Guaiacol, 3, 4
Guano, 42–43, 47
Guttmann's alumina packing, 52
Gypsum, 122–126
— effect on setting of cement, 115

H

Hack, 213
Hadfield's gyratory crusher, 92, 93
Half-value period, radioactive, 386
Hard finish plasters, 113, 116
Hardened glass, 267, 288
Hardening of plaster, 116
Harding's process for phosphorus, 446
Hauenschild kiln 111
Health hazards, asbestos, 319
— — in atomic energy research, 461
— protection against radiation, 462
Hedgehog rolls, 92
Heræus fused silica process, 301
Hessonite, 63
Hexaethyl tetraphosphate, 20*c*
Hexamethylene tetramine, 6
— para-amino-triphenylmethane, 9
High alumina cements, 133
— — — fineness, 133
— — — setting time, 133
— — — soundness, 134
— — — specific gravity, 134
— — — strength, 134
— — — resistance to shear, 134

High speed steel, 69
Hilbert and Frank's German process for phosphorus, 446
Hittorf's black phosphorus, 426
Hoffmann kiln, 80, 104, 232, 235
Hollow glass ware, 277
Holst drier, 84
Hoof meals, 39
Horizontal kiln, 230
Horn metals, 39
Horry rotary furnaces, 426
Hotop kilns, 105
Hubnerite, 343–344
Hyacinth, 63
Hydrargyllit, 50
Hydrated lime, 438
Hydration of cements, 117
— heat of, 119
— heat evolved on, 119
Hydraulic limes, 77, 78, 82–83, 119
Hydrochloric acid, germicidal value of, 3
Hydrocyanic acid, disinfecting properties, 11
Hydrofluoric acid, disinfecting properties of, 11
— — evolution in superphosphate dens, 30
Hydrofluorsilicic acid, disinfecting properties, 11
Hydrogen cyanide, 20*b*
— peroxide, disinfecting power of, 7
Hydroquinine, disinfecting properties of, 4
Hydroxide, potassium, 13; see also *Potassium hydroxide*
Hypochlorites, disinfecting properties of, 8, 9
— germicidal value of, 3

I

Ichaboe guano, 42
Illuminants, zirconia, 334
Ilmenite, 323, 324, 347
Impervite, 118
Incandescent mantle industry, 335 *et seq.*
Incendiary bombs, 71, 72
India, mica from, 324
Infra-red rays, opaqueness of glass to, 266
Insecticides, 17–20*a*
— selective, 20*c*
Insulating glass, 291
— porcelain, 202
Intermittent kilns, 79
Iodic hydrarg, 14
Iodine antiseptics, 3, 6, 10
— cyanide, 6
— trichloride, germicidal value, 3, 10
— uses of, 426, 427
— water, germicidal value, 3
Ionisation, connecting with disinfecting properties of, 10, 14
Ionium, separation of, 408
Iridescent glass, 288
Iron alloys, 70
— cistern cement, 147
— effect on glass, 295
— enamelled, 306
— estimation of, 119, 120
— in alum, 53, 57
— in bricks, 216
— in fire-clays, 246
— in magnetic separation of, 178
— ore cements, 112
— oxide, colouring earthenware with. 1 199
— pans, enamel glaze in, 147
— phosphate, 445
— Portland cement, 85
— salts, disinfecting properties of, 16
— silicides, 422
— work, protection of, 418
Ironite, 119
Isotopes, separation of, 410
Italian asbestos, 314
Itrol, 16

J

Japanese porcelain, 196
Jargon, 63
Jaubert process, 143
Jeffrey pulveriser, 93
Jena glass, 264, 269, 276, 291
Jenisch ball mill, 94
Jersey stone, 171
Jigger, vertical, 181
Johnstone kiln, 103, 104
Jolleying clay, 181
Joudrain's phosphorus process, 446
Juniper, use in polishes, 442

K

Kainite, use as manure, 40
Kankar, 78
Kaolin, 55, 155–156, 193; see also *Chi* *clay*
— chemical composition of, 149–152
— zeolite from, 59
Kaolinite, 156, 193
Keene's cement, 116, 130, 147
Keller furnace, 426
Kentish rag, 111, 119
Kent mill, 96
Keramo, 299
Keramyl, 11
Kettles, calcining, 115
Keystone lime kiln, 79
Kieselguhr, 173, 435, 439, 441

Kieserite, 41
Kilns, 79–81, 100–103, 109–112, 122, 228–236
— Aalborg, 111, 112
— archless, 228, 230
— Batchelor, 110
— bottle, 110
— brick, 228–236
— Bührer continuous, 221, 232, 235
— cement, 99–103
— clamp, 229
— continuous, 104, 231
— Dietzsch, 111
— dome, 110
— down-draught, 229, 246
— Dumesnil, 122
— for lime burning, 79–81
— for refractory goods, 246
— Gibbons, 110
— gypsum, 122
— Hauenschild, 111
— Hoffmann's, 231–235, 246
— horizontal, 230, 246
— Hotop, 111
— Johnstone, 110
— muffle, 206
— plaster, 122
— rotary, 99–103, 122
— Schneider, 111
— semi-continuous, 230
— shaft, 110
— Spackman's, 109
— Staffordshire, 236
— stage, 110
— stationary, 109–112
— stein-ribbed, 111
— up-draught, 230
Kish, 419
Krupp ball mill, 95
Kryolite—see *Cryolite*
Kunzite, 63

L

La Farge cement, 82
Laboratory glass, 264
Lactic acid, disinfecting properties, 35
Lagging cements, 143–144
— for steam-pipes, 143, 146, 318
Largin, 16
Lathe, for earthenware, 180
Lävenite, 355
Lawns, pottery, 178
Le Chatelier test, 133
Lead antimoniate, 175, 201
— arsenate, 20*a*
— compounds, use as fluxes, 173
— glasses, 275
— glazes, 173
Lead oxides in enamels, 307, 309
— — in glass, 271
Leather meal, 39
— jackets, 20*a*
Leguminoseæ, fixation of nitrogen by, 39
Lenix drive, 97
Lenses, manufacture of, 290
Lepidolite, 322
Libbey-Owens process for glass, 284
Light bulbs, 289
— frosting of, 289
— Ivanhoe machine, 289
— Owens machine, 289
— ribbon-type machine, 289
— Westlake or Kadon machine, 289
Lime, analysis of, 81, 119–125
— burning of, 79–81
— chemical analysis of, 127
— common, 77, 78–81
— composition, 81
— detection by dyes, 111
— disinfecting properties of, 13
— estimation of, 128
— fat, 81
— hydrated, 438
— hydraulic, 77, 78, 82
— in bricks, 216
— in enamels, 308
— kilns, 79–81
— lean, 81
— manufacture, 78–81
— manures, 41
— nature of, 77
— precipitate, 34
— rich, 81
— slaked, 78
— slakers, 80, 81
— stucco, 118
Lime-nitrogen, 37; see *Calcium cyanamide*
Lime-sulphur dips, 18, 19
— — washes, 18
Limestone, 78
— in clay, 153, 154, 215
— use as manure, 41
Limogeic enamel, 309
Liquid gold, 270
Litharge, use as flux, 173
Lithia mica, 322
Lithium aluminium silicate, 63
Loams, 146
Löhnert's compound mill, 98
Louisville cement, 86
Lucifer matches, 429
Luminous watch dials, 397
Lurgi cement roasting process, 107, 108
— sinter band, 107
— sinter grate, 108
Lustre glazes, 200
Lutes, 146–148
Lux's mass, 50
Lymphogranuloma venereum, 16*a*

M

Machines, soft mud, 220
Mack's cement, 117
Madras mica, 324
Magnesia, 137
— estimation of, 128
— in cement, 115
— in glass, 274, 279
— use in glaze, 172
Magnesia bricks, 249
— cement, 137
— mica, 323
— mixtures, 46
Magnesite, 137, 194
Magnesium aluminate, 63
— — bricks, 249
— chloride, 137
— limestone, 78
— oxychloride cements, 137 *et seq.*, 435
— peroxide, 7
— production by reduction with aluminium, 76*a*
— salts, 137
— — removal from water, 60
— silicofluoride, 129
Majolica, 163, 167
Malins, 156, 217
Manganates, disinfecting properties of, 7
Manganese alloys, 70
— metallic, 68, 70
— removal from water, 60
Manganese, use in glass-making, 276
— oxides, 189
— — colouring glass with, 295
— — — pottery with, 175
— permutit, 60
Mannheim calciner, 122
Mantles, incandescent gas, 335 *et seq.*
Manures, 21–47
— analysis of, 44–47
— certificates for, 47
— determination of nitrogen in, 45
— — of phosphorus in, 45
— incompatible, 42
— mixed, 41, 42
— moisture in, 45
— nitrogenous, 36–40
— statistics, 47
Marble, 78
— artificial, 139 *et seq.*
— cement for, 148
— Marezzo, 140
— Moreau, 141
Marezzo marble, 140
Margett's cement process, 89
Marls, 156, 217
Marquardt's porcelain, 195
Match manufacture, 453
Matches, 451–454
— after-glow prevention, 452
Matches, composition of, 451–454
— double dip, 452
— French State, 453
— "Lucifer," 451
— phosphorus, 451
— "Promethean," 451
— safety match compositions, 452
— safety, 452–454
— white phosphorus, 452
Meal, blood, 39
— castor oil, 38
— horn, 39
— rape cake, 38
Mealy bugs, 20*c*
Medina cement, 85
Medusa, 127
Melting temperatures of some glass ty
263
Mercuric bromide, 14, 15
— chloride, 3, 14, 15, 18
— cyanide, 15
— ethylene diamine sulphate, 15
— iodide, 15
Mercury, disinfecting properties of, 15
— oxycyanide, 15
— peroxide, 7
— salicylate, 15
— salts, 14–15
— vapour lamp, 303
— zinc cyanide, 15
Mesothorium, separation of, 409
Metal polishes, 441
Metallic salts, germicidal value of, 10
Metals, cements for joining to wood, 147
Methasan, 19
Mica, 321–326
— amber, 322
— artificial, 326
— dark amber, 325
— ground, 323, 326
— literature of, 321
— "Madras Green Clear," 324
— "Madras Green Hydrated," 324
— manufacture, 322
— powder, 323
— production of, 325
— scrap amber, 326
— sheet, 323
— silver amber, 325
— species of, 321
— synthetic, 325
— uses of, 324
Micanite, 324
Microsol, 14
Milch superphosphate den, 30
Milk, pasteurisation of, 7
— glass, 270
Mills, ball, 89, 93–94, 106
— Clark's, 89, 90
— colour, 191
— compound, 97, 98

Mills, edge-runner, 218, 219
— pug, 99, 178, 220
— roller, 93, 95, 96
— tube, 89, 96, 97, 107
— wash, 218
— wet grinding, 176
Millstones, 434
Mineral superphosphate, 31
Mites, 20*b*
Mixed manures, 41, 42
Mixers for slurry, 91
Mixing silos, 99
— slag, 84
Modelling clay, 179–181
Moisture, estimation of, 45
Molasses, removal of salt from, 60
Molitor ball mill, 94
Molybdenum alloys, 70
— metal, 68, 70
— molybdate, 46
Molybdic acid solutions, 46
Monazite, 327, 342
— sand, concentration of, 329
— — Wetherill separator for, 329
Monox, 418
Montanin, 11
Moorish ware, 167
Mordants, 51, 56, 57
Mortar, 125
Mortar cement, 125
— common, 125
Mosser cooler, 103
Moulding clay, 180
— porcelain, 197
Moulds for earthenware, 180
Moyer waterproofing process, 126
Muffle kiln, 208
Multi-chamber tube mills, 99
Muriate of potash—see *Potassium chloride*
Muscovite, 285, 287, 321
Mycobacterium tuberculosis, 16*a*
M.Y.L., 20*b*

N

Naphthol, beta, 4
Naples, yellow 165
Native guano, 43
Natrolite, 59
Neodymium, colouring porcelain by, 320
— use in glass, 320
— oxalate, 301
— sulphate, 301
Nernst filament lamp, 334
Nesfield triple tablets, 10
Neuclear reactors, 458
Neumann's process for phosphorus, 446
Neutral bricks, 233
Neutron reproduction in atomic piles, 458
Neutron moderators, 457
Newfoundland asbestos deposits, 282
Niagara Falls, 403
Nickel alloys, 70
— colouring glass by, 269
— use in glass making, 250
— oxide, 165
Nicol's spissograph, 124
Nicotine, 19
— disinfecting properties of, 19, 20
— sulphur dip, 19–20
Nifos T, 19
Nigerian monazite, 293
Niobium, 361, 365
— estimation of, 361, 366
Niran (Parathion), 19
Nitra lamps, 365
Nitragin, 40
Nitre cake, disinfecting properties of, 12
Nitric acid, disinfecting properties, 11
Nitrogen, fixation of, 327
— bacteria, use as manure, 39
— fixed, world production of, 48
— — consumption of, 48
— lamps, 364–365
— oxides, disinfecting properties of, 11
Nitrogenous manures, 36–40
Nitroguanidine, lime, 42, 427; see also *Calcium cyanamide*
— — analysis of, 38
— — use as manure, 37, 38
"Nitrolim," 427
Nitro-phosphate, 42
Non-slip stone, 129
"Norbide," 438
Normal glasses, 254

O

Ochre, 164
Oil of eucalyptus, 5
— shales, 158
Olivene, 63
Opal, 63
— glass, 295
Opaque glass, 276–292
Open mixers, 219
Optical glass, 289
Orangite, 328
— analyses, 328
Oriental amethysts, 63
Orthite, 342
Orthoclase, 171
Ortho-tolidine as colorimetric reagent, 8
Osmic acid, 11
Ovens, earthenware, 185–187
— improvements in, 191
— pottery, 185–187
Overburden, 217
Overglaze colours, 199

Overglaze decoration, 190
Owen's glass bottle machine, 281
Oxalic acid, use as polish, 441
Oxidising disinfectants, 6
Oxychloride, 9
Ozone, disinfecting properties of, 5, 6
Ozonic ether, 7
Ozonides, 6

P

Paint for iron-work, 404
Paludrine, 16
Pancreatine, 7
Paper sizing, 57
Paperstock asbestos, 318
Paraffin, use as a polish, 441
Paraform, 6
Paraformaldehyde, 6
Parian cement, 125
— porcelain, 164
— ware, 196
Paris green, 20*a*
Paris, plaster of, 121–125
Parker's cement, 85
Partition blocks, hollow, 243
Passow's slag cement, 84
Paste, 65, 292
Patent plate glass, 287
Paving blocks, 211
— stones, 139 *et seq.*
— tiles, 241 *et seq.*
Pearls, 63
— artificial, 65
— cultured, 65
— "paste," 65
Pegmatite, 161, 285, 324
Penicillin, 16
Penicillium notatum, 16
Pens, tantalum, 341
Pentachlorophenol, 19
Pepsin, 7
Perborates, disinfecting properties of, 7
Percarbonates, disinfecting properties of, 7
Perhydrol, 7
Peridot, 63
Permanganates, disinfecting properties of, 7
— removal from water, 61
Permasan, 19
Permutit, 59, 60, 61
— sodium, 60
Peroxide, hydrogen, 7
Peroxides, disinfecting property of, 7
Peroxol, 7
Persulphates, disinfecting properties of, 7
Peruvian guanos, 42
Petroleum, cements insoluble in, 147
Pettigrew's furnace, 421
Pharaoh's serpents, 69
Phenol, germicidal value of, 1–3
Phenol in dips, 20
— use as disinfectant, 4
Phenyl-salicylate, 3
Phlogopite, 321, 323
— uses of, 324
Phosphate glasses, 276
— rock plant, 28
Phosphates, crushing of, 24
— deposits of, 21–23
— estimation of, 45
— natural, 21–23
Phosphatic manures, 21–33
Phospho-nitrogenous manures, 33–36
Phosphoric acid, 31, 32
— — use in glass making, 276
Phosphoryl esters, 20*c*
Phosphorus, 443–449
— allotropic modifications of, 446
— amorphous, 446
— black, 447
— condensation of, 445
— condensation plant, 445
— furnace (Readman and Parker), 444
— — (Electric Reduction Co.), 445
— Harding's process for, 446
— Hilbert and Frank's German process for, 446
— Hittorf's black, 447
— hydrides, 452
— Joudrain's process for, 446
— matches, 451
— — white, 452
— Neumann's process for, 446
— occurrence, 443
— old process for, 443
— production in matches, 451
— properties of, 446
— — properties of, 447
— pyromorphic, 446
— Readman-Parker process for, 444
— recent developments, 446
— red, 447
— reduction of, 427
— scarlet, 448
— sulphides, 453
— uses of, 448
— violet, 447
— yellow, 447
— — properties of, 447
— white, 447
— — substitutes for, 452
Photographic glass, 291
Pig-iron, production of, 428
Pink glass, 295
— overglaze, 198
Pipeclay, 157
Pipe drain, 196
Pitchblende, 387
Placing ovens, 185
Panel glass, 278
Plants, foods for, 21

Plasmodium vivax infections, 16
Plaster cements, 86, 121–125
Plaster of Paris, 121–125
— — — action of glue on, 124
— — — analysis of, 128
— — — hardening by gum arabic, 124
— — — properties of, 124
— — — theory of setting, 124
— — — uses of, 172
Plasters, calcium, 121
— flooring, 121–124
Plasters, grinding, 123–124
— hard finish, 121–124
— hardening of, 124
Plastic bricks, plant for, 99, 223
Plasticity of clays, 152, 179
Plate glass, 264, 267, 283
— — figured, 287
— — manufacture, 286
— making machines, 182
— powders, 438–439
Platinum, colouring pottery with, 175
Plumber's cement, 147
Plutonium, 455
Pointed enamel, 310
Polishes, 441–442
— french, 442
— furniture, 442
— stove, 441
— shoe, 442
Polishing, 433
— materials, 138, 423, 433 *et seq.*
— mechanical methods of, 442
— powders, 440
— steel, 433
Polonium, separation of, 408
Polysius tube mill, 97
Polysulphides, disinfecting properties of, 13
Porcelain, 195–205
— Beleck, 198
— bodies, 196, 198
— casting, 199
— cement for joining metal to, 147
— Chinese, 188
— clays for, 155
— decoration of, 200–201
— definition of, 163
— electrical, 202
— glassy, 197, 198
— glazing of, 197, 200
— hard, 196, 198
— Japanese, 198
— manufacture of, 198–200
— moulding, 199
— raw materials for, 195
— throwing, 199
Porpora glass, colour of, 296
Portland cement, 87 *et seq.*
— — action of sea water on, 119
— — adulteration of, 119
— — analysis, 116, 127–129
Portland cement, clay for, 155
— — composition of, 115 *et seq.*
— — constituents of, 117
— — high early strength, 120
— — low heat, 120
— — moderate heat, 120
— — natural, 78, 86
— — properties of, 120
— — setting of, 117
— — specifications of, 129
— — sulphate resisting, 120
— — types of, 120
— — white, 120
Pot, glass-maker's, 280
Pot-metal colouring of glass, 293
Potash, consumption of, in agriculture, 40
— estimation of, 46
— in enamels, 310
— in glaze, 172
— manures, 40
— mica, 322
Potassium, estimation of, 46
— alum, 55, 56
— bichromate, 269
— carbonate, conversion into ammonium carbonate, 61
— — in glass making, 269, 279
— chlorate, conversion into ammonium chlorate, 61
— — use in glass making, 270
— — use as manure, 41
— chloride, manurial value of, 41
— chrome alum, 56
— cyanide, disinfecting properties of, 11
— hydroxide, disinfecting properties of, 13
— nitrate, in glass, 248, 253
— — manure, 41
— perchlorate, 61, 274
— permanganate, 7
— — germicidal value of, 3
— phosphate, 41
— salts, manures, 40–41
— — removal from water, 60
— silicate, use as manure, 41
— sulphate, use as manure, 41
— sulphide, fungicide, 18
— superphosphate, 42
Potter's wheel, 179
Pottery, 161–167
— classification of, 162
— furnaces, 186, 187, 192
— improvements in, 167
— properties of, 166
— varieties of, 166
Pouilly cement, 86
Powder, 420
Powder metallurgy, 431
Precious stones, 63–65
Precipitated phosphate, 28
Press, for earthenware, 181
Pressed glass, 261, 264, 287

Printing table, 190
Propionic acid, disinfecting properties, 5
Protargol, 16
Protectyl, 15
Prussian blue, 53
Psittacosis, 16*a*
Ptyalin, 7
Puddling clay, 157
Pug mills, 99, 178, 220
Pumice, 439
Pumice stone, 439
Purple of Cassius, 61, 109
Puzzuolana cement, 83, 85
Pyrethrum powder, 20*b*
Pyriat, 11
Pyrites in fire-clays, 246
Pyrogallic acid, germicidal value, 3, 4
Pyrogallol—see *Pyrogallic acid*
Pyrometers, 177
— cements for, 147
Pyrope, 63
Pyrophoric alloys, 343
Pyrophoric alloys industry, 343
Pyrozone, 7

Q

Quartz, 63, 194
Quartz glass, 299–304
— fused, chemical apparatus in, 301
Quartzite, Findling, 248
Quicklime, 78
— disinfecting properties, 13
— use as manure, 41
Quinol, disinfecting properties, 4

R

Radioactive constants, 401
— emissions, 399
— ores, occurrence of, 390, 412
— series, 402
— substances, 399
— — uses of, 411
Radioactivity, induced, 403
— intensity, measurement of, 404
— theory of, 400
Radiothorium, separation of, 409
Radium, separation of, 407
Rags, use as manure, 39
Rails, testing joints of, 72–75
— welding by, 72
Ram pumps, 89
Ramie fibre, use in incandescent mantles, 335
Ransome's artificial stone, 144
Rape cakes, 38
Rape seed meal, 38
Rathenau furnace, 423
Raw cement flour, 98
Raw cement meal, 98
Readman-Parker phosphorus process, 444
Recuperators, 107
— section of, 106
Red bricks, 216
— burning clays, 157, 170
— glass, 295
— lead, as flux, 173
— — in enamels, 311
— — in glass, 275
— overglaze, 199
— phosphorus, 447
— spiders, 20*b*
Refractoriness under load test, 135
Refractory bricks, 214
— clays, 157
— concrete, 134
— materials, 173, 245–251, 421
Reinforced concrete, 118
— glass, 287
Resorcin, disinfecting properties of, 34
Retarders of setting of plaster, 16
Retorts, gas, 247
— graphite, 420
— lutes, 145
Riddled guano, 42
Rideal-Walker carbolic acid coefficient, 1
Ring roll mills, 25
Robbia ware, 167
Rock crushers, 24
— crystal, 63
Roller mills, 26, 93, 95, 96
Rolls, toothed hedgehog, 92
Roman alum, 55
Roman cement, 85–86
Room, disinfection of, 12
Roscoelite, 393
Rosendale Portland cement, 86, 87
Rotary crusher, 86, 92
Rotary kiln, 80, 99–103
— — fuel requirements, 103
— — plaster, 114–115
— weigher, 108
Rottenstone, 439
Rouge, 174, 434, 438, 440
Rouge flambé, 174, 202
Roulette mill, 96, 97
Rubbers (bricks), 157
Ruby, artificial, 52, 64
— Balas, 63
— natural, 63, 64
— reconstituted, 64
— thermite slag, 75
Rudersdorf kiln, 80
Ruggles-Coles drier, 83
Rumford kiln, 80
Rupert's drops, 265
Russian asbestos, 314
Rust, joint cement, 119, 146
— removers, 420
Rutile, 347

S

Saccharin, antiseptic properties, 6
Sack fillers, 108
Sackur's glass, 291
Safflowers, rouge from, 440
Sage plaster cement, 86
Sagger clays, 157
Saggers, 187
Saint Gobin glass, 264
Salicylic acid, disinfecting properties of, 5
Salol, 5
Salophen, 5
Salt, antiseptic properties of, 14
— glaze, 162, 195
— use in glass making, 273
— use as glaze, 172, 207
— use as manure, 41
Saltpetre superphosphate, 42
Salufer, 11
Samarskite, 327, 361
Sand, 173, 434, 438
— definition of, 154
— for sand-lime bricks, 239
— in clay, 154
— in glass, 278
— paper, 438
— use as abrasive, 440
Sand blast, 288
— cement, 113
Sand-lime bricks, 239
Sand moulding, 244
— paper, 439, 440
Sand's silica glass process, 299
Sandarac, 441
Sandstone, millstones of, 434
— use as abrasive, 438
Sang de Bœuf, 174
Sanitary ware, 167, 207 *et seq.*
— — enamelled, 305
Sanitas, 5, 6
Santobrite, 19
Santophen-20, 19
Santorin earth, 82, 83
Sapphires, artificial, 52, 63, 64, 65
Scab destroyers, 19
Scagliola, 130
Scale insects, 20*c*
Scheelite, 367
Schenk's scarlet phosphorus, 448
Schmatolla's kiln, 81
Schofer kiln, 79
Scholefield brick machine, 224
Schroeder red phosphorus, 448
Schwerin electrical purification of clay, 153
Scoop-wheel, 89
Scott's cement, 83
— selenitic cement, 83
Scrap mica, 324
Screen separators, 28
Screw press, 35, 172, 173
Sea water, action on cement, 111–112
— — use as manure, 43
Seediness of glass, 260
Seger's ruby glass, 267
Selenium, colouring glass with, 295
— in glass, 276
Semi-continuous kilns, 230
Semi-dry process for bricks, 224
Separators, 28
Serpentine asbestos, 282
Setting of cement, 85, 105, 117, 131
— of plaster of Paris, 124
Setting ovens, 185
Severin glass bottle machine, 282
Sèvres ware, 200
Sewage, disinfection of, 8–9
— sludge as manure, 42, 43
Shaft kilns, 104
— soot, 39
Shales, 158
— alum, 154
— oil, 158
Sheep-dips, 18–20
Sheet glass, 278–284
— — crown, 276
— — fluted, 276
— mica, 323
Shellac, use in polishes, 440
Shells, 78
— use as manure, 41
Shenstone fused silica process, 299
Ships, disinfection of, 12
Shoddy, manurial use of, 39
Shoe polishes, 442
Shrinkage of clays, 152
— — earthenware, 184
Sidero cement, 120
Sienna, 74
Sievert's glass machine, 284
Silica, 63
— bricks, 248
— chemical constitution of, 255
— cyclic structure of, 255
— detection by dyes, 111
— estimation of, 127
— for glass, 269
— fused, 299
— properties of, 300 *et seq.*
— tridymite from, 249
— use as manure, 41
Silica glass, 300 *et seq.*
— — properties of, 300
Silica-free glasses, 277
Silicates, 63
— Asch's theory of, 253 *et seq.*
— chemical composition of, 253
— lutes and cements for acids, 146
— manurial value of, 41
Silicofluoride, waterproofing plasters by, 119
Silicol process, 143
Silico-phosphoric acid, 445

Silicon, 422
— bonds, 255
— carbide, 414, 437; see *Carborundum*
— literature, 413
— monoxide, 417, 418
— properties of, 422
Sillimanite, 150
Silos ,cement, 98, 99
— mixing, 99
Siloxicon, 416, 418
Silundum articles, 417
Silver, colouring glass with, 295
— — pottery with, 175, 201
— citrate, disinfecting properties of, 16
— fluoride, disinfecting properties of, 16
— lactate, disinfecting properties of, 16
— nitrate, disinfecting properties of, 16
— overglaze, 200
— phosphide, 447
— salts, disinfecting properties of, 16
— stain glass, 295
Sizing paper, 57
Skin meal, 39
Slag, blast furnace, 83
— blocks, 140
— cement, 83–85
— drying, 83–84
— granulating, 83
— sand, 83
Slaked lime, 78
Slates, 148
Slip, 88, 169, 176, 177
Slop moulding, 220
Slurry, 88, 176
Smelting practice, modern, 76
Smidth cooler, 102
Snelus cement, 85
Soaking, 188
Soaps, aluminium, 57
— disinfecting properties of, 13
— use as lutes and lubricants, 147
— use as polish, 440
Soda—see *Sodium carbonate*
Soda, caustic—see *Sodium hydroxide*
— in enamels, 310
— in glass making, 270
Sodium 2.4-Dichlorophenoxy-acetate-monohydrate, 19
Sodium alum, 56
— aluminate, 50, 51, 52, 56
— arsenic, disinfecting properties of, 20
— arsenite, disinfecting properties of, 20
— bisulphate, disinfecting properties of, 12
— — germicidal value of, 3
— borofluoride, 11
— carbonate, in glass making, 270, 276
— — removal from water, 60
— cyanide, disinfecting properties of, 11
— fluosilicate, 20*b*
— hydroxide, disinfecting properties of, 13
— hydroxy mercury benzoate, 15
Sodium hypochlorite, disinfecting pr of, 8–9
— nitrate, uses of, 36–37
— paratungstate, 349
— pentachloro-phenate, 19
— permanganate, 7
— permutit, 60
— peroxide, disinfecting properties of, 7
— salts, removal from water, 60
— silicate, 142–148
— — cements, 144, 435
— — manure, 41
— — waterproofing by, 125
— silicofluoride, waterproofing by, 125
— sulphate, for glass, 310
— titanium sulphate, 328
Soft mud machines, 220
Soils, 158
Solid sodium aluminate, 56
— solutions, 150, 253
Solo mill, 98
Soluble glass, 142–145; see also *Sodium silicate*
— superphosphate, 31
Soot, analysis of, 39
— use as manure, 39
Sorel cement, 137, 138, 435
— — uses for, 138
Spackman kiln, 110
Spanish ware, 167
Specific gravity, determination of, 127
— — of slips, 177
Sphene, 348
Spinel, 63, 64
Spogumene, 63
Sprengel pump, 353
Spun glass, 265
Staffordshire kiln, 236
Stained glass, 295
Stains (earthenware), 168
Stamp mills, 26
Stannic oxide, use in glasses, 175
Staphylococcus aureus, 16
Stassfurt deposits, 40
Statistical analysis, 275
Statuary porcelain, 164
Steam boiler gauges, glass for, 293
— joints, amounts for, 146
— pipes, lagging for, 143–146
Steatite, 194
Steel, chromium, 69
— crushed, 438
— — use as abrasive, 438
— enamelled, 308
— manganese, 70
— melting by thermite, 72
— molybdenum, 70
— tool, 70
Sticking up earthenware, 182
Stiff-plastic process for bricks, 222–224
Stilbite, 59

Stills, ammonia—see *Ammonia stills*
Stock bricks, 213
Stone-breakers, 92
Stones, artificial, 139
— Cornish—see *Cornish stone*
— in glass, 260
— precious—see *Precious stones*
— Ransome's artificial, 144
— reconstructed, 140
Stoneware, 207–212
— chemical, 209
— culinary, 209
— fine, 208
Stove polishes, 441
"Strass," 65, 292
Streptomyces aureofaciens, 16*a*
Streptomycin, 16*a*
Striæ in glass, 260, 286
Stringiness of glass, 286
Stuart's granolithic stone, 139
Stucco, 18
Sturtevant Newaygo separator, 27
Sublamen, 15
Sugar industry, use of permutit in, 60
Sulphanilamide, 16
Sulphate, estimation of, 127
Sulphate of alumina—see *Aluminium sulphate*
— of ammonia—see *Ammonium sulphate*
— of potash—see *Potassium sulphate*
Sulphides, estimation of, 127
Sulphites, disinfecting properties of, 13
Sulphonamides, 16
Sulphur, disinfecting properties of, 13
— dioxide, disinfecting properties of, 12–13
— estimation of, 127
— fungicidal value of, 17–18
— fungicides, 17
— in cement, 109
Sulphuric acid, disinfecting properties of, 12
Sulphurous acid, disinfecting properties of, 12–13
Super cement, 120
Superheated steam water, action on glass, 268
Superphosphate dens, 30
— manufacture, 28–32
— plant, 28–32
— statistics, 47
Surface clays, 158
— hardening, 127
Swimming baths, disinfection of, 9
Swing-jaw stone-breaker, 92
Syphilis, 15

T

Table glass, 242, 251
Tachiol, 16
Tafelglas, 251
Tannic acid, use as stove polish, 441
Tantalic oxide, 337
Tantalite, 361
Tantalum, 361
— estimation of, 361
— metallic, manufacture and properties of, 362
— — lamps, 375
— — uses of, 363
— ores, distribution of, 361
Taps, stoneware, 210
Tartaric acid, 5
T.C.P., 4
Teeth, artificial, 205
Tellurium colouring glass, 297
Tender clays, 158
Tensile strength, estimation of cement, 127
Termites, 20*a*
Terra-cotta, 162, 242 *et seq.*
Testalin, 57
Testing raw materials in pottery, 175
Tetraethyl-pyrophosphate, 19, 20*c*
Tetramethyl-thiuram-disulphide, 19
Textile industry, use of tungsten in, 349
Thermal syndicate process, 300
Thermit, for demolition, 76
— for incendiary bombs, 75
— for welding and fabrication, 76
— mode of ignition of, 75
Thermite, 67–75
— alumina from, 52
— bombs, 71, 72
— fire, 71
— heat of reaction, 71
— slag, 75
— steel, 75
— use as heating agents, 71, 72
— welding rails by, 72
Thermometers, glass for, 265, 270
Thiophosphites, 453
Thiurad, 19
Thomas-Gilchrist furnaces, bricks for, 249
— — process, 32, 33
— phosphate, 32, 33
— slag, 32, 33
Thoria, 332
— effect of cerium dioxide on emissivity of, 335
— purification of, 330
Thorianite, 328
— composition of, 328
Thorite, 327, 328
— analyses, 328
Thorium, 327
— extraction of, 330
— industrial utilisation of, 335
— minerals, analysis of, 333
— natural occurrence, 327
— nitrate for mantle manufacture, testing of, 339

Thorium ores, occurrence of, 341
— physical properties of, 334
— preparation of metallic, 332
— radioactivity of, 334
— solubilities of, 331
Thrips, 20*c*
Throwing clay, 180
— porcelain, 199
Thuringen glass, 264, 269
Thymol, use as disinfectant, 4
Tiles, 167, 212, 241, 242
— encaustic, 241
— glazed, 242
— literature, 241
— paving, 241
— roofing, 241
— tests for, 212
Tin alloys, 70
— chloride, colouring pottery with, 125
— oxide, 200
— — colouring glass with, 297
— — in enamels, 310
— — in glazes, 175
— pinks, 175
Tincal, 172
Titanium, 347
— industrial utilisation of, 349
— ores, analysis of, 351
— preparation of metallic, 348
— properties of, 349
Tobacco dips, 20
— extracts, 20
Tobacco-sulphur dips, 19–20
Tooth-powders, 420
Toothed hedgehog rolls, 92
Topaz, 63
Totenhaupt's phosphorus, 448
Tourmaline, 173
Town refuse, use as manure, 42, 43
Trass, 82, 83
Tremolite asbestos, 313–319
Trials, 177
Tribromonaphthol, 4
Triformal, 6
Tripoli powder, 434, 439, 440
Tube mills, 24–25, 89, 96, 97, 98, 107
Tubing, glass, 278
Tumblers, glass, 283
Tungsten, 367
— colloidal filament, 378
— drawn wire filaments, 378
— extraction of, 368
— in industry, 369
— lamps, 376
— ores, analysis of, 371
Tunnel drier, 100, 227
— kiln, 187, 191
— ovens, 185
Turner's cement, 147
Turning clay, 180
Turquoises, 63

U

Ultra-violet light, opaqueness of glass
244
— — — sterilisation by, 372
Underglaze colours, 200
— painting, 190
Unglazed pottery, 162
United States asbestos deposits, 314
Uralite, 144
Urals, asbestos in, 314
Uranium, 387
— metallic, manufacture of, 388
— ores, distribution of, 388
— utilisation of, 389
Uranothorite, 328
Urea, ammoniacal fermentation of, 37
— from calcium cyanamide, 37
Urine, phosphorus in, 443
Urotropine, 6
Uviol glass, 291

V

Vanadinite, 393
Vanadium, 393
— and compounds in industry, 396
— extraction from its ores, 394
— metallic properties of, 395
— ores and alloys, analyses of, 397
Vases, 167
Vassy cement, 86
Venetian glass, 264, 296
Verbundglas, 291
Vermiculite, 325
Verneuil's blowpipe, 64
Vertical jigger, 181
— kilns, 109, 111 *et seq.*
Vicat needle, 132
Victoria stone, 139
Violet glass, 295
Vitreosil, 299–304
— electric immersion heater, 300
Vitrifiable clays, 159
Vitriolised bones, 32

W

Ward's stone, 139
Ware, sanitary, 169–193, 207 *et seq.*
— shaping of, 179–184
Wash leather, 440
— mill, for cement, 87, 88
Waste products, use as manure, 40
Watch dials, enamelled, 310
Water, disinfection of, 8–9

Water, removal of alkali from, 61
— — of calcium, 60
— — of gold from, 61
— — of iron from, 60, 61
— — of magnesium from, 60
— — of manganese from, 60, 61
— — of potassium from, 60
— — of sodium from, 60
— sterilisation by permutite, 61
Water-glass, 41, 142–148; see also *Sodium silicate*
Waterproofing cement mortar, 126
— — concrete, 126
— cloth, 57
Wedging of slip, 178
Welding by "thermit," 71, 76
Wet fish scrap, 34
— grinding, 88, 89, 176
Whale meal, 36
Wheeling forced feed washer, 92
Whirlers, 174
White bricks, 217
— clays, 170, 174
— glass, 265
— — opaque, 276, 292
— lead, in enamels, 311
— — use of flux, 173
— overglaze, 200
— Portland cement, 120
— sulphate of alumina, 54
— ware, 209
Whiting, use as glaze, 172
— use as polish, 154
Whole guano, 36
Wiborgh phosphate, 32
Window glass, 273, 278
Wire cut process for bricks, 221
Wöhlerite, 355
Wöhler phosphorus process, 445
Wolframite, 367
Wood, cements for joining metal to, 147
— fireproofing, 57
Wool, injury by sulphur-lime dips, 19
— waste, use as manure, 39

X

X-rays, glass for bulbs, 277
Xylolite, 138

Y

Yellow clays, 159, 170–176
— glass, 295
— overglaze, 200
Yttrialite, 342
Yttrotantalite, 361

Z

Zeolites, 160
— artificial, 59, 60, 61
— carbonaceous, 61
— complete exchange, 61
— natural, 59
— synthetic, 61
Zinc alloys, 70
— chloride, disinfecting properties of, 16
— — germicidal value of, 3
— dimethyl-dithio-carbamate, 19
— oxide, in enamels, 310
— — in glass, 266
— — in glazes, 175
— oxychloride cement, 138
— peroxide, 7
— salts, disinfecting properties, 16
— sulphate, disinfecting properties, 16
— sulphide, luminous preparations with radium, 397
Zircon, 63
Zirconia bricks 249
Zirconium, 355
— analyses of typical minerals, 357
— extraction of metallic, 356
— industrial utilisation, 356
— ores, geographical distribution of, 355
— silicate, 63
Zirkelite, 355
Zschimmer's glass, 291

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE, * MYSORE. *
LIBRARY

Checked.
Raj 17/8/55.

7/7/93

21/5/82

C. F. T. R. I. LIBRARY, MYSORE.

Acc No. 3215
Call No. F8 N54·2

13/6/80

Please return this publication on or before the last DUE DATE stamped below to avoid incurring overdue charges.

Due Date	Return Date	Due Date	Return Date
20/3	18/3		
16.1.86	6/1		
7/6/97	6/6		

CHECKED
2008

VERIFIED
2013

CFTRI-MYSORE
3215
Industrial and m..

Call No. F8 N54.2
Author MARTIN
Title Industrial and
Manufacturing -
-Chemistry. Edn. 6.
Vol II
Acc. No. 3215